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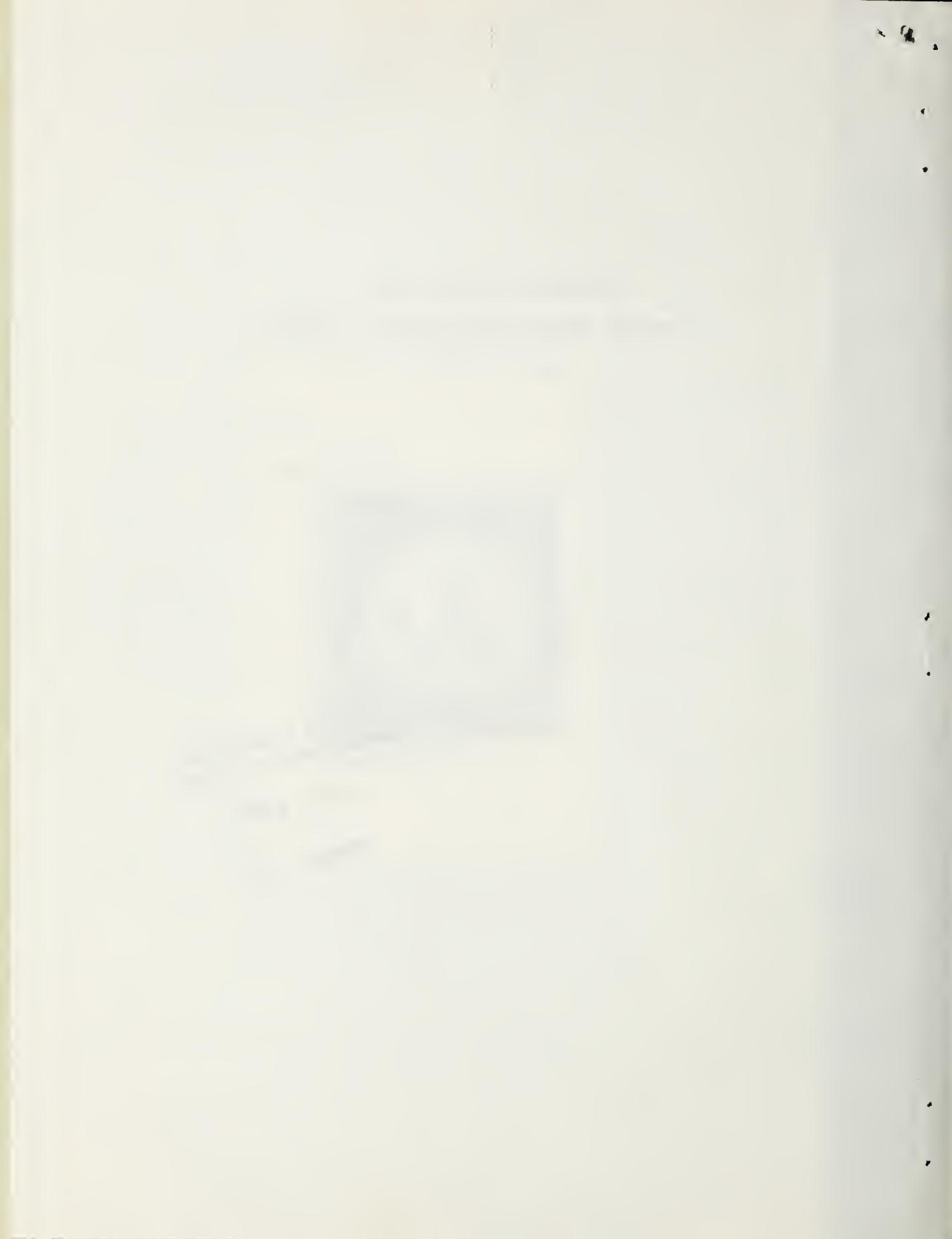


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## 15TH TEXTILE CHEMISTRY AND PROCESSING CONFERENCE

May 5-7, 1975

## THE TEXTILE INDUSTRY AND ITS RESPONSE TO THE "GROWING" ENERGY CRISIS

St. Clair J. Tweedie

Assistant Director

Economic Consulting Services

Wolf and Company

Washington, D. C.

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Cotton Textile Processing Laboratory, SRRC

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## THE "GROWING" ENERGY CRISIS

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In recent months, especially since the lifting of the Arab oil embargo, many in this country have questioned whether there is, in fact, a petroleum shortage and, in turn, an energy crisis. After reading mountains of reports, studies and articles and listening to countless speeches, I am more convinced than ever that the crisis is real. However, I am also convinced that hasty actions and radical solutions can only compound the very real difficulties associated with developing sound, comprehensive and long-range solutions to this very complex set of problems.

The energy crisis did not begin with the Arab oil boycott nor did it end when available supplies increased relative to reductions in world demand. The nature of the energy crisis is much broader and much more fundamental. We are dealing with an array of economic, technological, social and political considerations associated with the way in which we develop and consume the world's non-renewable natural resources. What was once nearly free is now costly. People in many developing countries had natural resources which were developed, exported and consumed by foreigners, but they had no power. Today they have achieved considerable power.

The crisis, in the short run is economic. Energy in all forms has become increasingly expensive. Oil consuming nations have experienced large dollar outflows to producing nations. Individuals, in this country, have been forced, because of higher prices and relatively little change in real incomes in the last year or so to shift their consumption expenditures in favor of energy. Industries have seen energy assume major proportions relative to other production costs. It is now quite clear that the era of cheap and abundant energy has passed forever.

What I have attempted to do thus far is to provide a glimpse, from my own perspective, of the nature of the problems that those of us who have been so intimately involved in the textile industry's energy programs have had to take into consideration. With your indulgence I should like to develop this line of thinking a bit further.

Energy historically has been an essential ingredient of economic growth. The correlation between energy growth and expansion of Gross National Product (GNP) is positive and highly significant. Further, changes in the level of GNP and the level of employment have been closely linked in the United States. It is not difficult then, to predict the impact of energy supply shortages or bottlenecks on GNP and the labor force.

Energy requirements, overall, have been increasing quite rapidly. On the other hand, domestic production has been nearly flat for several

years now. The difference has been made up by imports. Based upon what we know about the time and cost of developing existing energy resources as well as new and exotic ones, it is highly unlikely that domestic energy production will change significantly over the next half dozen years or so. Therefore, as a result of past energy policies and practices we seem to have little choice but to live with rapidly rising petroleum imports between now and the early 1980's. We cannot, however, depend upon the continued availability of petroleum imports with any degree of certainty.

Industry is the largest single user of energy in this country. As such, it will be most severely impacted by shortages. What can industry do to minimize the impact of any such shortages? The obvious answer is conservation -- improve the productivity of energy.

The Textile Industry's Approach. To give a bit of perspective to how the textile industry responded to it, it is necessary to consider just how much energy the industry consumes. Textile manufacturers consume about 2.8 percent of the purchased fuels and electric energy required by all major industry groups surveyed by the Census of Manufactures. This breaks down accordingly -- 33.5 percent is electric power; 40.7 is natural gas; 25.6 percent is oil; and only .2 percent is coal.

The bulk of electric power is consumed in spinning, weaving, knitting, and carpet and rug production. Natural gas is consumed primarily in dyeing and finishing operations -- nearly 60 percent. Fuel oils are used for heating, steam generation and machinery lubrication.

Textile producers, like other industrialists and individuals had for many years taken an abundant supply of energy for granted, but early in 1973 it became apparent that government and petroleum industry leaders' increasing concerns about the nation's need to conserve scarce energy resources had reached crisis proportions.

Through ATMI, early in 1973, by means of the association's newsletter, in speeches by industry leaders and other communications textile management was alerted to the serious nature of the problem. Discussions were held with major industry trade publications in an effort to build support for an industry-wide effort to meet whatever problems might arise in the future.

At the Fall '73 Board of Directors meeting, ATMI organized an Energy Policy Committee. Mr. Roger Milliken of Deering Milliken, Inc. was selected to chair that committee. The committee's membership consists of a blend of chief executive officers and top engineering executives from almost all of the major textile firms in this country. The committee held its first meeting in Washington on November 8. It immediately launched a program designed to alert the industry and its million employees to the need for

conservation and to convey to the federal government the industry's dependence upon a reliable supply of electricity, gas and oil for energy and petrochemicals.

Immediately following the meeting, the Energy Policy Committee sent the President a telegram pledging the industry's cooperation in conserving energy. The telegram also emphasized the need for industry to have a high priority in allocation programs in order to safeguard jobs. Copies were sent to Secretary of Commerce Dent and Federal Energy Administrator Simon, because of their respective roles in the energy area. Similar telegrams were sent to the governors of textile states with the suggestion that key industry officials meet with state energy officials.

A two-pronged program was launched. One facet was to encourage development of a specific and detailed energy conservation program in every plant. This started with a commitment from top management to conserve energy in every way possible. Virtually every company made such a commitment. Careful studies of existing manufacturing techniques were made and steps taken immediately to improve energy consumption efficiency where this could be done without reducing production or employment.

In addition, massive education programs were conducted to show individual employees how they personally could contribute to energy conservation both on and off the job.

A second phase of the ATMI energy conservation program was the development of a formula for measuring energy conservation. This was done so both individual manufacturers and the industry as a whole could measure progress and pinpoint those areas where more conservation might be realized.

The energy conservation-efficiency measure works in this manner. A formula was developed to measure the number of BTU's required to produce a given amount of stock. Data was gathered from individual companies over the period from November 1972 to December 1973 to provide a 12-month base. The current month-by-month energy input per pound of production was then compared to the base period in order to measure progress.

While this formula is not completely precise, it does provide a useful measure of energy-efficiency. It shows that conservation programs conducted by the textile industry have resulted in approximately 10.0 percent reduction in fuel consumption.

Our experience with the energy problem indicates that conservation through more efficient use is the area where industry can make a contribution toward the national goal of self-sufficiency in the next 7 to 10 years.

The textile industry's outstanding record of voluntary conservation has been recognized throughout the government and by many leaders of industry as an outstanding example of what needs to be done. It was a proud moment for the textile industry when on last October 16 the president of ATMI was invited to the White House to explain that ATMI energy efficiency measurement program. Leaders of the biggest seven energy consuming industries were asked by the Secretary of the Interior to take a look at the textile industry's program and see how it could be adapted to their respective industries.

The successful energy conservation programs already functioning at the company level are just a beginning. Thermostats have been turned down, driving speeds reduced, eliminated steam and heat leaks and geared machines to run at the most efficient speeds. The next step is to come up with more sophisticated and innovative -- and more expensive ways to reduce the amount of energy needed to produce a yard of cloth.

Money, talent and energy can, and are, being spent in a number of areas which will be productive in terms of increased energy-efficiency. These include:

- Development of technically sound and economically justifiable means of reclaiming heat from exhaust of textile drying and curing processes.
- Recovery of chemicals used in textile processing.
- Development of new dyes and finishes which require less energy for application to textile fibers.
- Use of solvents other than water which vaporize at lower temperatures and lower energy consumption rates.
- Development of more efficient waste treatment methods and better ways to dry fabrics.
- Finding new processing techniques which reduce the number of times which fabrics must be washed and dried during processing.
- Development of techniques to convert waste materials into fuels or other useful products.
- Development of practical means to reduce the energy required to maintain required atmospheric conditions in spinning and weaving plants.
- Development of methods to reduce the solar heat load on buildings in summer; and increase it in winter.
- Develop ways to use excess heat generated by manufacturing processes.

-- Determine the feasibility of combining complementary manufacturing operations so that one process could effectively use waste products from the other. This could be done by locating a textile finishing plant adjacent to a power generating station and utilizing the hot water effluent from the power plant in textile processing.

-- Development of both consumer products and industrial process machines which lower lifetime energy requirements. Examples of this are soil resistant textile finishes.

-- We could try to develop small-scale means to use solar energy; or processes which require lower water and air processing temperatures; or processes which will allow lower air volumes to be used.

-- Something quite basic would be better insulation for our buildings.

Looking down the road toward 1980 the textile industry's energy requirements can be seen to be increasing as population and consumer demands grow. It is estimated that the total energy equivalent of 39.7 million barrels of oil consumed by the textile industry in 1973 will grow to 52.5 million barrels by 1980. This is an increase of more than 32 percent. The extent to which this projected increase can be reduced without reducing projected production will be determined in large measure by how successful the industry is in developing more efficient ways to utilize energy.

#### CONCLUSION

Unfortunately energy conservation and efficiency measures alone will not solve this nation's, and the textile industry's energy problems. However, conservation and the accelerated use and availability of electricity -- generated by coal and nuclear fuels -- do offer a solution. By expanding the use of coal and nuclear power this country can reduce its dependence on imported oil. With a greatly expanding electrical energy base the remaining supplies of oil and natural gas can be conserved for those applications for which no substitutes exist.

The leadership of the textile industry has realized this for some time and has become quite active in promoting a sound national energy policy embodying these elements.

## IMPROVED DRAWFRAME BLENDING

C. L. Shepard, R. S. Brown, and L. J. Richard  
Southern Regional Research Center

The blending of cotton and manmade fibers can be initiated in either the opening, the carding, or the drawing operations. Many textile men consider the drawframe the ideal location because the most efficient processing organization for each type fiber can be utilized through carding and the wastes are kept separate. Unfortunately, blending at the drawframe has certain serious drawbacks. The slivers do not blend homogeneously during the drawing process but rather form separate fiber channels within the output sliver. This lack of fiber homogeneity becomes very apparent after dyeing, resulting in a reduced quality fabric. Because of this problem research was conducted to develop processing techniques to improve fiber homogeneity with drawframe blending.

## Experimental Blending Devices

A back folding device, Figure 1, was developed which superposes the cotton sliver on the manmade sliver in the back drafting zone. This device and subsequent action

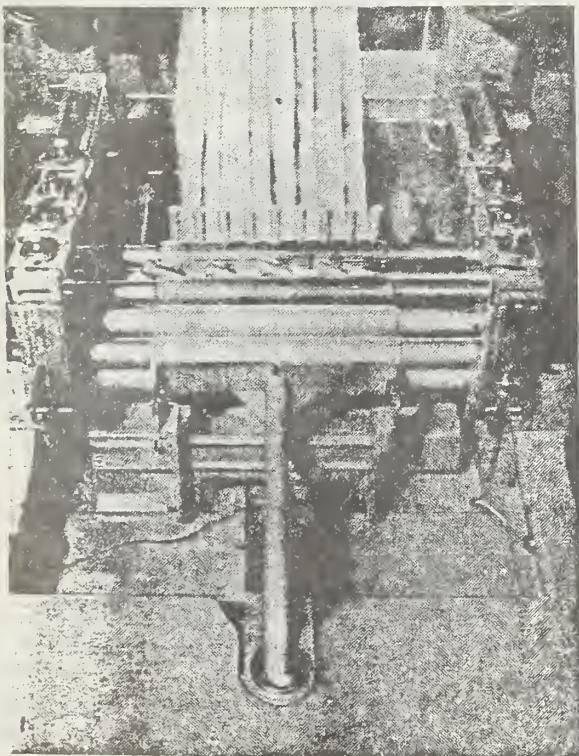


Figure 1

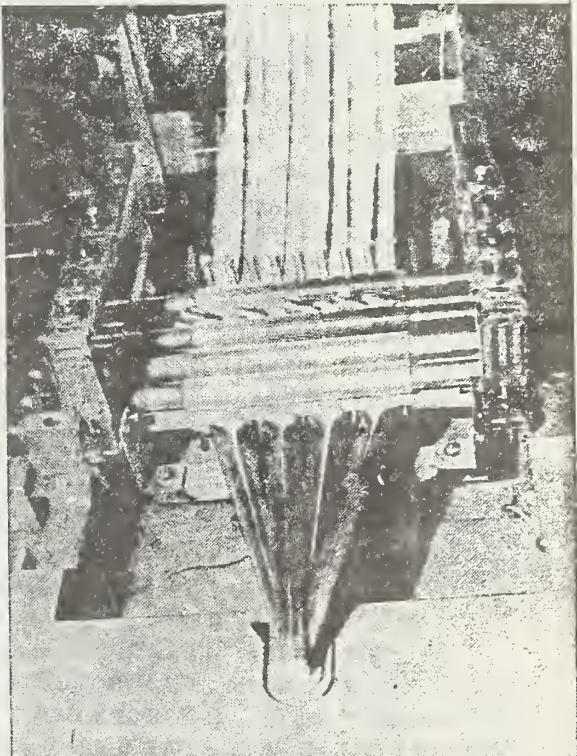


Figure 2

enabled the fibers to be drafted and blended together in the middle and front zone. The fibers are removed in the form of four cotton/manmade ribbons using the conventional fly control pan assembly.

An additional front folding device to further increase fiber homogeneity was developed to complement the back folding device, Figure 2. This mechanism converts the four ribbons leaving the front drafting roll into superposed layers before entering a rectangular trumpet which condenses the layer of ribbons into a composite sliver.

#### Photographic Technique

A rapid and inexpensive method has been developed for evaluating fiber homogeneity in blends. Blended sliver and roving samples are threaded in a special holder, heated and sliced to expose a cross-section of the blended fibers. The heat treatment changes the color of the cotton fibers to a light brown while leaving the manmade fibers white. Color microphotographs of the cross-sections were produced with a sterozoom microscope equipped with a Polaroid camera.

#### Yarn Evaluation Procedure

All tests for evaluating the experimental folding devices were processed on a single delivery drawframe using a 4 over 4 drafting system with fluted top and bottom rolls. Test organization included two experimental and one standard condition for blending fibers at the drawframe. The two experimental tests were run separately using the back folding device with and without the front folding device. All tests were replicated twice. Blend level for all tests was 50/50 carded cotton/polyester. The properties of the cotton and polyester fibers are listed in Table I. Blending and drawing organization consisted of two processes, eight ends each process, 65 doublings. The folding devices were used in the first drawing process for the experimental tests, and standard drawing arrangement was used for all other processes. Drawframe data is listed in Table II. Second drawing sliver, weighing 55 grains/yard, was processed into 1.0 hank roving. Four different yarns, 12/1, 18/1, 24/1, and 30/1 were processed for each condition.

#### Evaluation Results

Figures 3, 4, and 5 are black and white reproductions of color microphotographs from second drawing sliver. It should be noted tones and contrast are lost in these reproductions. The darker shades are the cotton fibers and the lighter shades are the polyester fibers. Figure 3 shows conventional



Figure 3



Figure 4



Figure 5

TABLE I - FIBER PROPERTIES

FIBER	VARIETY	GRADE	STAPLE	MICRONaire
				DENIER
COTTON	DELTAPINE	M	1-1/16"	4.52
POLYESTER	KODEL	421 SD	1-1/2"	1.50

TABLE II - DRAWFRAME DATA

CONDITION	FIRST DRAWING		SECOND DRAWING
	STANDARD	EXPERIMENTAL FOLDING DEVICES	
DRAFT			
FRONT ZONE	2.79	2.79	2.79
MIDDLE ZONE	2.14	2.14	2.14
BACK ZONE	1.41	1.41	1.41
TOTAL	8.50	8.50	8.50

SPACING (IN.)

FRONT ZONE	1-5/8	1-5/8	1-5/8
MIDDLE ZONE	1-5/8	1-5/8	1-5/8
BACK ZONE	1-5/8	2-1/4	1-5/8

TABLE I and TABLE II

blended sliver, Figure 4 shows blended sliver using the back folding device, and Figure 5 shows blended sliver using the back and front folding device. Differences between blending conventionally and with the folding devices can be easily detected, while differences in the homogeneity of the blend between the two experimental folding devices are less apparent.

A complete analysis of yarn processed with and without the folding devices has been made. Representative data from these tests are presented in Figures 6, 7, 8, and 9. Referring to Figures 6 and 7, little or no difference in count strength product for yarn skein strength and single strand strength was found between blending conventionally or with the folding devices. Although the data indicates the largest variations occur within the 30/1, the differences are statistically insignificant. Referring to Figures 8 and 9, the coefficient of variation within the yarns, the roving, and the sliver vary slightly between conventional and experimental blending; however, the differences are not significant.

#### Additional Blending Process

Fiber blend homogeneity can be improved by increasing the draft at first drawing and increasing the doublings at second drawing. The first drawing process with both conventional and the back folding device were investigated with the total draft changed from 8 to 16. Second drawing organization con-

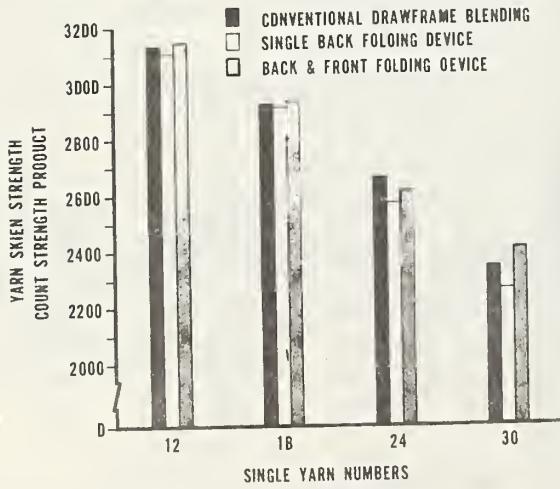


Figure 6

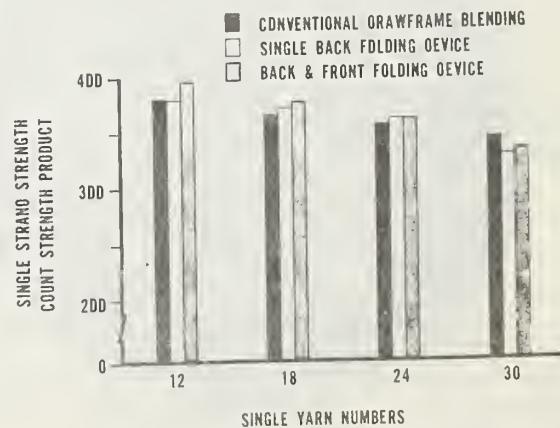


Figure 7

sisted of 16 ends, 8 total draft, for a total of 128 doublings. Second drawing sliver was processed into yarns using the same organization as previous tests.

Visual inspection of the color microphotographs indicate improvement in blending homogeneity over first and second drawing sliver processed with the folding devices using 64 doublings. An analysis of the yarn processed with this method indicated significant improvements in yarn properties for the 12/1 and 18/1 yarns over conventional and back folding blending methods. No significant improvement over conventional or experimental back folding blending was noted for the 24/1 yarns. Results from 30/1 yarns indicated decreased yarn properties compared to yarn processed with conventional and back folding blending methods.

### Conclusion

Fiber homogeneity of 50/50 carded cotton/polyester blended sliver was significantly improved with the experimental back and front folding devices. A comprehensive study of four yarn sizes revealed little or no differences in yarn properties which indicates no fiber damage occurred within the experimental blending process. Additional fiber blend homogeneity can be achieved using the back folding device with increased draft and doublings, although caution is advised when spinning fine yarns.

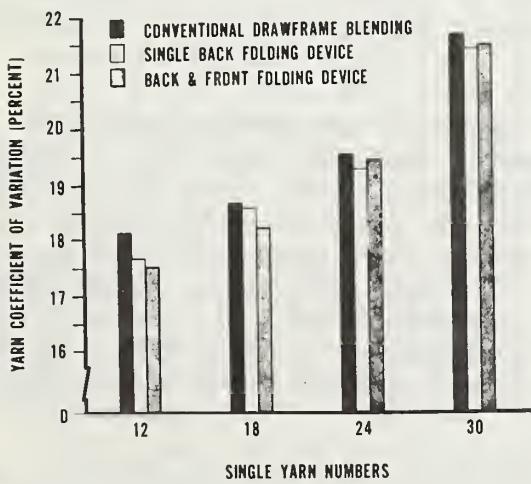


Figure 8

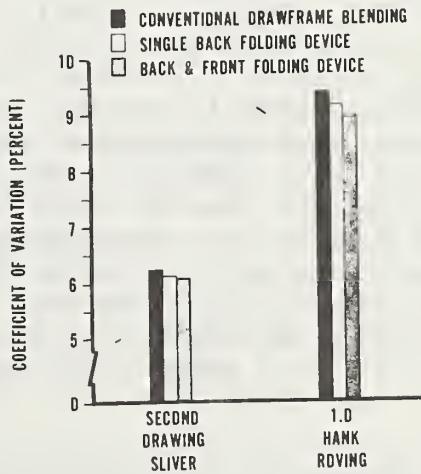


Figure 9

INTERRELATIONSHIPS AMONG CARDING PARAMETERS,  
COTTON/POLYESTER BLENDS, AND PROCESSING PERFORMANCE

by

Jack Simpson and Louis A. Fiori  
Southern Regional Research Center

Fabrics made from blends of cotton and polyester have many desirable qualities that would be lacking if the fabrics were composed of only one of the fibers. Cotton adds comfort, water absorption, and the natural look, while the polyester contributes strength, abrasion resistance, and easy care properties.

Whether to blend cotton with polyester in the opening/picking operations or at the drawing process is in most cases dependent on the type fabric being produced. Generally, for cross dyed fabrics a more homogeneous blend can be obtained by blending in the opening room and taking advantage of the mixing action of the card.

The objective of this research was to determine the conditions required to process cotton/polyester opening room blends most efficiently.

#### RESULTS AND DISCUSSION

While there have been many studies relating the stress-strain properties of the polyester and cotton fiber (the high modulus polyester fiber has double the stress and triple the elongation of the cotton fiber and is similar in the cotton stress-strain range) to their blended yarn and fabric strengths few have dealt with the processing efficiency of the blends, especially carding. We have found that the main fiber properties that foretell carding efficiency are shear friction, compression, and compression recovery characteristics. Table I lists the shear friction and compressibility data for various cotton/polyester blends. For both the 1.5 and 2.25 denier polyester blends the compression and compression recovery height increased with increased polyester content. This should increase cardability; however, the shear friction also increased with increased polyester content and this should greatly hinder cardability. The shear friction for the 2.25 denier polyester blends was slightly less than that for the 1.5 denier blends.

Figure 1A shows the effect of blend level (1.5 denier) on the cylinder load and card sliver short term variability and 1B the effect on card web neps. Cylinder load increased with increased polyester in the blend. This decreased the carding action, which increased the short term sliver variability

and the neps in the cotton component (1B). The latter is shown by placing the neps in the blended card web on a 100% cotton basis.

To reduce the cylinder load for high polyester content blends, mills increase the flat to cylinder setting.

Figure 2 shows the effect of flat setting and carding rate on the cylinder load and card web neps for 65c/35p and 50c/50p blends using the 1.5 denier polyester. Although increasing the flat setting did reduce the cylinder load,

Table I  
SHEAR FRICTION AND COMPRESSIBILITY DATA FOR THE VARIOUS BLENDS

Blend	Shear Friction ( $S \times 10^{-4}$ )	Average Compression Height (in.)	Average Recovery Height (in.)
100% C	1.98 (1.98) <sup>a/</sup>	3.00 (3.05)	4.20 (4.23)
80c/20p	2.37 (2.59)	3.02 (3.11)	4.20 (4.19)
65c/35p	3.00 (3.23)	3.09 (3.11)	4.27 (4.28)
50c/50p	3.72 (3.94)	3.11 (3.20)	4.32 (4.39)
35c/65p	4.63 (4.96)	3.18 (3.31)	4.34 (4.38)
100% P	5.06 (5.22)	4.30 (3.61)	5.25 (4.55)

a/ Results for the blends using the 1.5 denier polyester (8)

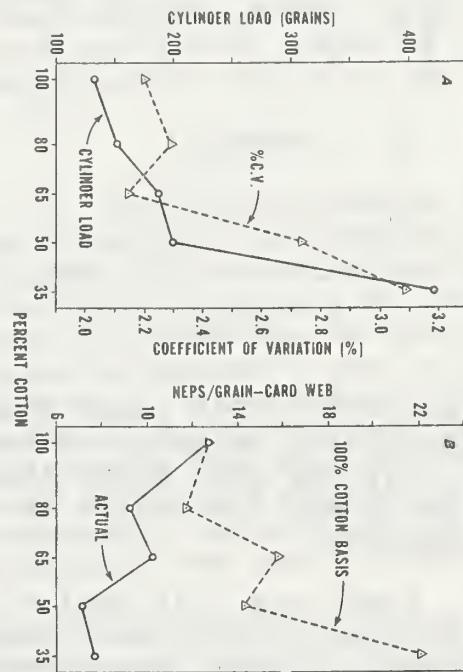


Fig. 1

it also increased the neps in the card web. The reason for the increase in neps with the increase in flat setting is that the flat teeth have less carding contact with the fibers. It is therefore apparent that the high friction of the polyester causes the cylinder load to increase and the carding action to decrease as more polyester is added to the blend. Increasing the flat setting to offset this will reduce the cylinder load but it will further decrease the carding action causing an increase in the neps of the cotton component.

The yarns from the lots were knitted and woven into fabrics and (1) cross dyed with a bright yellow color for the cotton and a blue for the polyester; (2) cross dyed with the bright yellow for the polyester and the blue for the cotton; (3) union dyed with a blue color. While the improvement in quality of the fabric from the close (.010 inch) flat setting over that

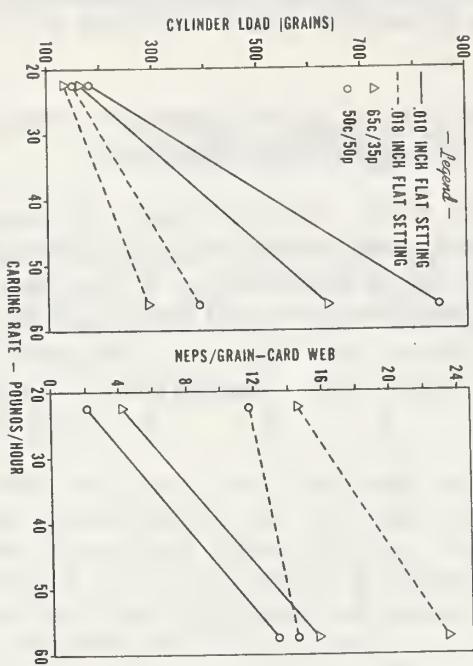


Fig. 2

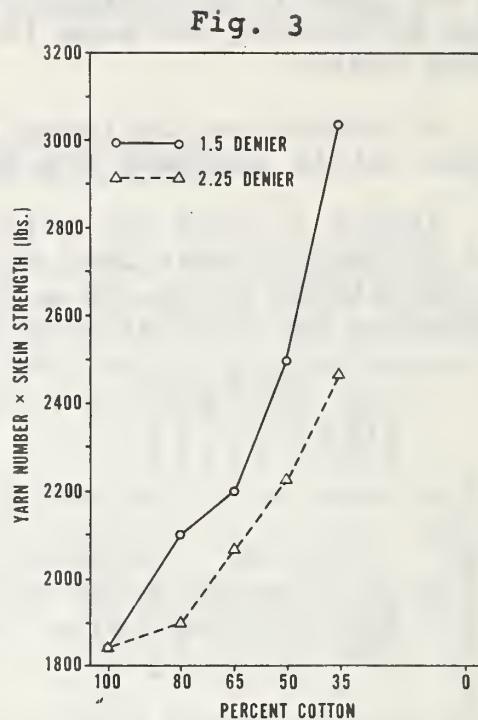


Fig. 3

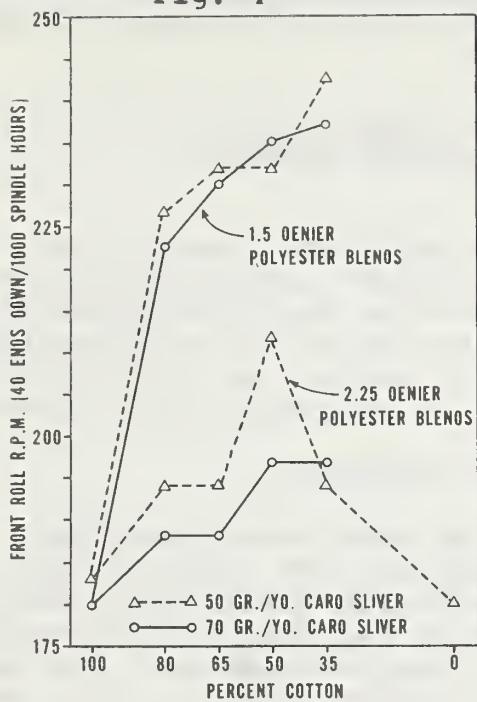
of the wide (.018 inch) flat setting could be observed in all three dyeing methods, it was most clearly evident by method (1). It was also found that increasing the polyester content in the blend did little to improve the yarn grade or fabric appearance.

Since the 2.25 denier polyester is coarser and the blends of it with cotton have lower shear friction than the 1.5 denier polyester blends, they should yield lower cylinder loads. This was found to be true.

Figure 3 shows the effect of blend level and denier on yarn strength. For both polyester deniers yarn strength increased with each increment of polyester added to the blend.

Thus, unlike the regular modulus, where over 50% polyester has to be added to the blend to get an increase in strength over the 100% cotton, small amounts of polyester added to the blend with this medium staple carded cotton, gave significant improvements in yarn strength. The strength of the yarns from the blends of the 2.25 denier polyester was less than those of the 1.5 denier polyester. This difference became greater as the percentage of polyester in the blend increased. The effect of blend, denier, and sliver weight on the spinning speed (front roll rpm at constant spindle speed of 13,000 rpm) of a 36/1 yarn for a constant end breakage rate of 40/1000 spindle hours is shown in Figure 4. For the 1.5 denier polyester blends a

Fig. 4



small addition of polyester to the blend resulted in a large increase in spinning speed which leveled off with further additions. With the 2.25 denier polyester blends, a moderate increase in spinning speed occurred followed by a decrease with the addition of polyester to the blend. This evidently resulted from the fewer fibers per cross section for the relatively fine yarn 36/1 yarn used in this study. This coarser denier would be more appropriate for a coarser yarn.

#### SUMMARY

This investigation demonstrates that if opening room blends of cotton and polyester are used, then a high percentage cotton blend can be processed more efficiently than a high

percentage polyester one. The reasons for this are as follows:

1. The friction of the polyester caused decreased cylinder to doffer fiber transfer as its percentage in the blend increased. This increased the cylinder load and decreased the carding action necessary for the cotton component, causing an increase in the short term card sliver variability and neps in the cotton component.
2. While the mill practice of increasing the flat to cylinder setting with the addition of polyester reduced the cylinder load, it further reduced the carding action needed by the cotton component causing an increase in card web neps.
3. While the use of a coarse denier polyester in the blend reduced the cylinder load and neps to some extent, it lowered the improvement in spinning speed that would be obtained with a finer denier polyester in the blend.
4. Increasing the polyester content in the blend did little to improve the yarn grade regardless of the denier used.
5. With the use of high modulus polyester, yarn strength and elongation increased with each addition of polyester to the blend. There was not the usual decrease in yarn strength until more than 50 percent polyester was added, as happens with regular modulus polyester.
6. A small addition of 1.5 denier polyester to the blend (20%) made possible a very large increase in spinning speed while holding end breakage constant.

Acknowledgments: The authors express their appreciation to Miss Reba Lawson, USDA, ARS, Cotton Quality Spinning Laboratory, for the shear friction tests.

ANALYTICAL TECHNIQUE FOR DETERMINING ROVING  
QUALITY FROM COTTON/POLYESTER BLENDS

by

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In a recent investigation<sup>1</sup> on the blending techniques of cotton and polyester fibers, a Uster Evenness Tester was used as an analytical tool to investigate the effects of roll settings and back drafts on roving quality. This presentation shows some of the results of this investigation, illustrated by case history examples.

MATERIALS AND METHODS

The four blends used in this investigation were 80c/20p, 60c/40p, 50c/50p, and 30c/70p (c = medium staple cotton; p = 1.5 inch, 1.5 denier polyester). Second and third drawing slivers of 55 grains per yard were used. The sliver of each blend was processed through a Saco-Lowell Rovematic roving frame into 1.0 hank roving with 27 different combinations of roll-settings and back drafts as follows:

Front-to-Middle Roll Setting (in.)	Middle-to-Back Roll Setting (in.)	Back Draft
2 ) For blends of 80c/20p,	1-5/8	1.6
2-1/8 ) 60c/40p, and 50c/50p	1-7/8	2.0
	2-1/8	2.3
2-1/8 ) For blend of 30c/70p	1-5/8	1.6
	1-7/8	2.0
2-3/8 )	2-1/8	2.3

Additional hank rovings of 0.7 and 2.0 were studied on the 50c/50p blend. Each of these rovings was put on 10 bobbins with 150 yards per bobbin, and were tested on the Uster Evenness Tester at 25 yards per minute. The criteria for roving quality judgement based on the Uster were: coefficient of variation, Spectrogram characteristics, and recorder diagram characteristics.

Figure 1 shows a Spectrogram and two segments of a "synthesized" recorder diagram. The shaded hump shown in the Spectrogram indicates a drafting wave due to loss of fiber control in the drafting system. Drafting waves could be caused by the roll speed, roll weighting, roll setting and draft. In this study, the caustic factors were confined mainly to roll settings and drafts, since they were the main variables under

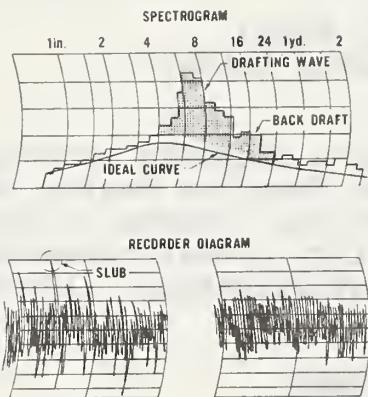


Fig. 1

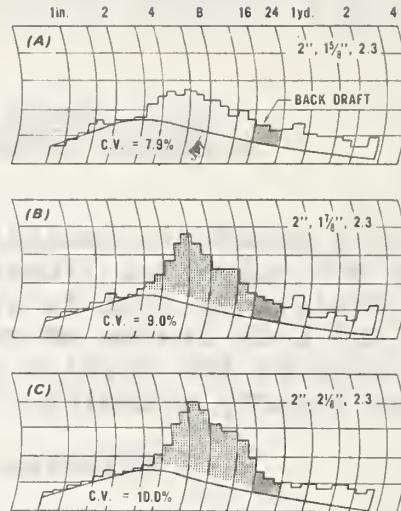


Fig. 2

investigation. Cyclic effect caused by the back draft zone on roving is traceable by the portion of the Spectrogram between the 16 and 24 inch marks (the dark area) when producing a 1.0 hank roving from 55 grains per yard sliver having a back draft of 1.6. Similarly, any cyclic effect caused by the front draft zone would be reflected by the left portion of the Spectrogram up to the 16 inch mark.

#### RESULTS

A great number of Spectrograms and recorder diagrams were obtained and analyzed. But only selected samples are being presented herein to illustrate how the Uster Evenness Tester helped in selecting the best combinations of draft zone variables which produced the highest quality roving for the four blends within the limits studied.

A typical Spectrogram set is shown in Figure 2. It represents three 1.0 hank rovings made from an 80c/20p blend using the same front roll setting of two inches, back draft of 2.3, but three different middle-to-back roll settings, namely, 1-5/8", 1-7/8", and 2-1/8". A mere increase of 1/4" in the middle-to-back roll setting from 1-5/8" caused an enormous drafting wave in the roving as indicated by the shaded part of the Spectrogram in Figure 2(B). Further increase of the middle-to-back roll setting to 2-1/8" caused the drafting wave to become more prominent. Meanwhile, the C.V.'s increased from

7.9% to 9.0% and 10.0%, respectively. Many more similar cases will be shown during the presentation.

Another phase of the investigation dealt with the relationship of roving and yarn in which the same yarn size was spun from three different sizes of rovings. These rovings were free of drafting waves and slubs. Figure 3 shows a 1.0 hank roving having a 5.7% C.V. was spun into a 36/1 yarn with a 20.2% C.V., while a 2.0 hank roving having a 7.6% C.V. was spun into a 36/1 yarn with a 20.0% C.V. That difference of total spinning drafts (36 vs. 18) did not seem to affect the final yarn evenness is attributable to the high quality rovings used in spinning.

### CONCLUSIONS

The Uster Evenness Tester provides three of the major criteria for judging roving quality: (1) coefficients of variation; (2) Spectrogram characteristics revealing drafting waves; and (3) recorder diagrams revealing possible slubs undetectable visually. Using these criteria collectively should lead toward producing quality rovings.

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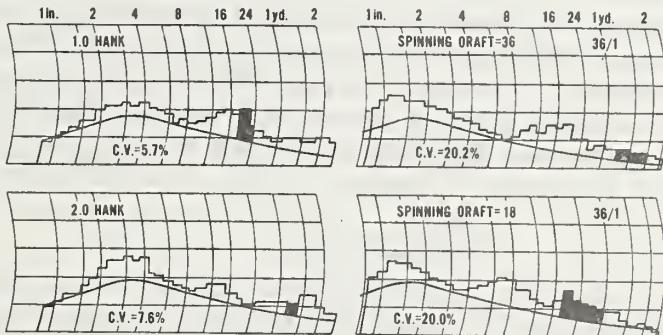


Fig. 3

## SELECTION OF OPTIMUM FIBER PROPERTIES FOR COTTON KNITS

by

G. F. Ruppenicker, Jr., E. C. Kingsbery, and N. A. Bouquet  
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Cotton knitting yarns should be smooth, uniform, and as free from neps and other imperfections as possible. Because of these rigid requirements, it is important that the cottons used to produce knitting yarns be carefully selected. Knitting emphasizes yarn irregularities, whereas in woven fabrics the interlacing of two yarn systems tends to minimize unevenness. Short term yarn irregularity or frequent thick and thin places will cause an undesirable cloudy effect in a knitted fabric, and long term variation may show up as horizontal stripes or barré in a weft knitted fabric. Slubs, knots, and other yarn imperfections can seriously reduce knitting efficiency and also detract from fabric appearance. Large imperfections can damage the fine knitting elements, causing the machine to knit irregular fabric.

For many of the traditional knitted cotton fabrics, yarn strength may be considered to be of secondary importance, since the knitting machines used for such products can knit fabrics from relatively weak yarns, and the emphasis is often on softness and appearance. However, with the development of higher speed knitting machines and the growth of the knitted outerwear market, strength requirements for knitting yarns have changed. Modern, fine gauge warp and double knitters need premium quality, high strength yarns to operate efficiently.

Cotton fiber properties will vary considerably depending upon the variety, growing conditions, and other production variables. In this report, the effects of fiber fineness, strength, and length on the properties of cotton and cotton-polyester blend knitting yarns and knitted fabrics will be presented. Properties of yarns and fabrics made from blends of cotton containing both regular and high tenacity polyester fibers are discussed.

## EXPERIMENTAL

Five quality cottons, strict low middling or better, were selected for the study. Fiber properties of the cottons are given in Table I. The five were so chosen that, by judicious pairing, the effects of fiber fineness, fiber strength and fiber length could each be determined independently of the others. Thus, the effect of fiber fineness was determined by pairing the two cottons that were about the same in strength and length but differed in fineness. Similarly, the effect of fiber strength was obtained by pairing the two cottons that differed primarily in strength and the effect of length from two cottons that differed mainly in staple length. The average strength cotton was used in both the fiber strength and fiber length comparisons.

The cottons were processed into both carded and combed yarns. The blended

yarns were produced from drawframe blends in proportions of 80% cotton-20% polyester and 60% cotton-40% polyester. Both the regular and high tenacity polyester were 1½" staple and 1.5 denier. Processing conditions were based on a survey made of knitting industry practices. All yarns were spun from double creel roving. Carding was done at a production rate of 8 lbs./hour.

TABLE I. FIBER PROPERTIES

COTTON	Fine	Coarse	High	Average	Short
	Fiber	Fiber	Strength	Strength	Staple
GRADE	Strict	Strict	Strict		Strict Low
	Middling	Middling	Middling	Middling	Middling
<b>LENGTH:</b>					
Classer's (in.)	1-1/8	1-3/32	1-3/32	1-1/16	31/32
<b>Digital Fibrograph:</b>					
2.5% Span Length (in.)	1.14	1.10	1.12	1.11	.93
50% Span Length (in.)	.50	.51	.51	.49	.41
Uniformity Ratio	44	46	46	44	46
MICRONAIRE READING	3.9	5.2	4.8	4.8	5.1
<b>TENACITY:</b>					
Stelometer, 0-gauge (g./tex)	43.6	42.5	48.1	39.1	38.1

To establish twist-strength relationships, yarns with twist multipliers ranging from 2.8 to 4.8 were spun from the cottons and cotton/polyester blends. However, only those yarns with twist multipliers of 2.8, 3.2, and 3.6 were used to produce knitted fabrics. Most cotton knitting yarns would fall within a twist multiplier range of from 2.8 to 3.6; however, slightly higher twists may be desirable for warp knits and some double knits. Plain jersey and rib fabrics were knit from the yarns.

The fabrics were evaluated in the grey, bleached, and resin-treated states. Bleaching was done in tubular form in a dye beck, using a solvent scour and hydrogen peroxide bleach. The fabrics were dried under relatively tensionless conditions. Selected fabrics were given a light shrinkage control finish which consisted of a 5½% solids solution of a modified glyoxyl based resin plus a polyethylene softener. Fibers, yarns, and fabrics were tested in accordance with standard procedures (1, 2).

## RESULTS

Since all five cottons selected were of good quality, most of the yarns produced were of above average uniformity and had a relatively low number of neps and imperfections. Table II shows uniformity data as measured by the

Uster Evenness Tester for 18/1 and 30/1 carded yarns. Compared with the Uster experience values for yarn irregularity, which are shown at the bottom of the table, all the yarns except the 30/1 spun from the short fiber cotton were of better than average uniformity. The fine fiber cotton produced the most uniform carded yarns. Combed yarns showed similar results.

TABLE II. UNIFORMITY OF CARDED COTTON YARNS

COTTON	EVENNESS C.V. (%)	
	18/1	30/1
Fine fiber	13.9	17.8
Coarse Fiber	15.1	18.8
High Strength	14.1	18.7
Average Strength	15.1	18.8
Short Staple	18.7	23.2
Uster Average	19.8	22.6

Table III shows the single-strand break factors for 18/1 and 30/1 carded and combed yarns spun from each of the cottons. Yarns spun from the fine cotton averaged about 10% stronger than those spun from the coarse cotton. This is mainly because the fine cotton has more fibers per cross sectional area for a given yarn size. Yarns spun from the high strength cotton were about 20% stronger than those spun from the average strength cotton. However, the average strength cotton produced yarns over 40% stronger than the short staple cotton. Combing resulted in an additional 10 to 15% increase in yarn strength for most of the cottons.

TABLE III. YARN STRENGTH

COTTON	SINGLE STRAND BREAK FACTOR (No. x Oz.)			
	Carded		Combed	
	18/1	30/1	18/1	30/1
Fine Fiber	289	276	334	311
Coarse Fiber	263	256	303	271
High Strength	312	272	348	316
Average Strength	252	233	287	266
Short Staple	176	164	-	-

Yarns produced from the cotton-polyester blends were generally slightly more uniform and higher in grade than the all-cotton yarns. The strength properties of the blend yarns varied considerably depending upon the type of polyester and, to a lesser extent, upon the properties of the cotton. Yarns spun from blends containing regular tenacity polyester, which has a breaking tenacity in the general range of most cottons, were usually weaker than the 100% cotton yarns. This is due primarily to the large difference in elongation between the two fibers (6 to 8% for cotton compared to over 30% for the regular tenacity polyester). Those spun from blends containing the high tenacity polyester, which had a lower elongation (about 20%) than the regular polyester and was considerably stronger than the cotton fiber, were

significantly stronger than the all cotton yarns.

Blending either type polyester with cotton had a tendency to lower the twist required for maximum yarn strength. This was a desirable trend because of the lower twists used for most knitting yarns. One of the areas where a small percentage of polyester fibers was found to be quite useful was in spinning low twist knitting yarns from a relatively short staple cotton. By using a blend containing only 20% high tenacity polyester, spinning performance was greatly improved and yarn strength increased.

### FABRICS

Table IV shows the effects of cotton fiber properties on the bursting strengths of gray fabrics produced from each of the cottons. Differences in yarn strength due to fiber fineness were insignificant in the knitted fabrics; however, fabrics knit from the high strength cotton were from 15 to 27% stronger than those knit from the average strength cotton. The average strength cotton produced fabrics that were from 30 to 35% stronger than those knit from the short staple cotton. Differences in strength were still apparent in the finished fabrics despite substantial strength losses from the resin treatment.

TABLE IV. BURSTING STRENGTH OF GREY COTTON KNIT FABRICS

COTTON	BURSTING STRENGTH (lbs.)			
	Carded		Combed	
	18/1	30/1	18/1	30/1
Fine Fiber	110	82	119	90
Coarse Fiber	101	82	120	82
High Strength	124	86	144	93
Average Strength	101	73	113	80
Short Staple	78	54	-	-

Bursting strengths of fabrics knit from the blends followed the same trends as yarn strengths; however, strength losses due to resin treatment were much less for the blended fabrics than for the all cotton fabrics. Resistance to abrasion was improved considerably by the addition of 20 to 40% polyester fiber.

The lengthwise shrinkage of the bleached fabrics was reduced significantly by the addition of polyester fiber. The resin treatment also reduced the shrinkage tendency of the fabrics. However, after resin treatment there was very little difference in shrinkage between the 100% cotton fabrics and those containing the polyester fibers. Widthwise, most of the fabrics showed a slight growth tendency after laundering.

### CONCLUSIONS

Significant improvements in the quality and strength of cotton knitting yarns can be obtained by carefully selecting cottons based on fiber properties.

Blending small percentages of polyester with cotton can further improve yarn uniformity and strength. Knitted fabrics produced from cotton-polyester blends generally had better abrasion resistance, less shrinkage, and smaller strength losses due to resin treatment.

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## FROM TUFTS TO YARN, AN INTEGRATED TEXTILE PROCESSING SYSTEM

by

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## HISTORY AND BACKGROUND

For many years the SRRC Cotton Textile Processing Laboratory has been cognizant of the fact that for significant improvements to take place in cotton textile processing, fundamentally new techniques and radically new equipment must be developed (1).

In 1967 a pioneering program was initiated to obtain basic information necessary for the development of new, efficient techniques for processing cotton fibers into yarn. The research included the study of aerodynamic, electrostatic, acoustical, and mechanical forces for manipulating, separating, blending, and individualizing cotton fibers. Studies were also made to determine the effect of these forces on the physical properties of the cotton fiber (2,3). Cotton Textile Processing Laboratory scientists proposed an integrated textile processing system wherein textile fibers could be transformed from tufts to yarn within a single machine, a system that would eliminate manual handling and would function without contaminating the mill atmosphere.

Utilizing findings from the basic studies (4,5,6) and with the goal of a continuous, integrated processing system as the ultimate objective, development projects were geared to investigate and develop practical applications for use in a future experimental processing system. From this research, fundamental system components emerged (7,8,9). The most promising hardware developed was assembled into an experimental system in which fibers could be processed from tufts to yarn. Although the goal of perfecting a commercially acceptable concept which meets OSHA standards lies in the future, a functional experimental system has been assembled and is now the subject of this paper. Hereinafter it will be referred to as the "system."

## FIBER PREPARATION - STAGE I

The system, Figure 1, is an integrated conglomerate of many unique functions

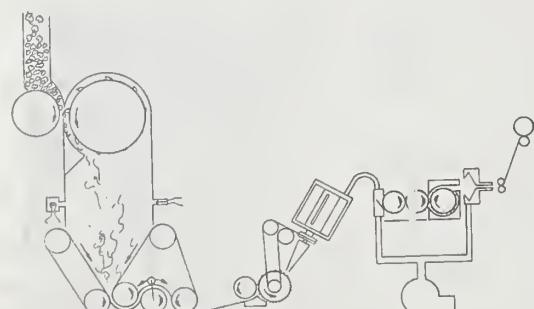
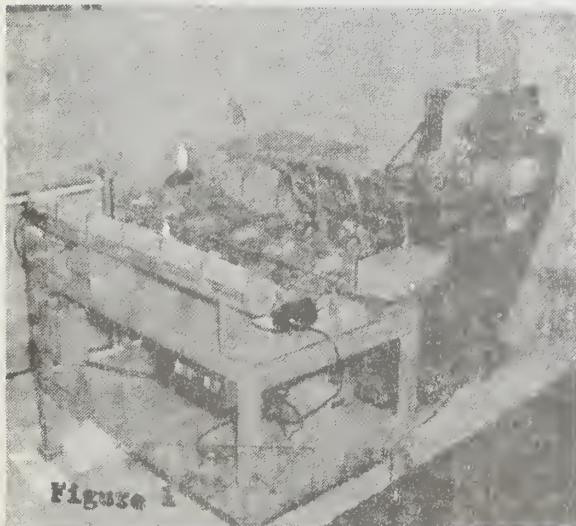


Figure 2

wherein fibers can be processed from tufts to yarn. It is shown schematically in Figure 2. Stage I incorporated initial opening, cleaning, and lap formation.

Tufts from blending hopper feeders or from an SRRL Bale-Opener-Blender (10,11) are fed into a vertical chute or hopper which is separated from a second lower chute by an initial opening apparatus. This opening means transforms relatively large tufts ranging in weight from .5 to 1.5 grams into small tufts from .03 to .04 gram. The apparatus is composed of a resilient feed cylinder that oscillates as it rotates and a processing cylinder equipped with retractable teeth. The teeth protrude from the peripheral surface of the cylinder for approximately half of each revolution. The processing cylinder is self doffing and generates a negligible volume of air during operation. This is extremely beneficial in that turbulence is eliminated and tufts are permitted to gently fall and settle in the lower chute uninfluenced by external forces other than gravity. The reciprocating motion of the feed cylinder prevents "grooving" thereby enhancing feed uniformity.

To insure a non-varying tuft density in the lower chute, a minimum height is continuously maintained by means of an electronic sensor which controls the first stage opening feed cylinder on an "on-off" mode of operation. Tufts in the lower chute are supported by conveying belts that converge. The belts are integral parts of a low force lap-forming apparatus that transforms the lower chute tuft column into a continuous fibrous mass closely resembling a standard picker lap but possessing a lower coefficient of variation.

The theory of operation involves the compression of the fibers and tufts between two belts and a small displacement (movement) of one belt in relation to the other. The movement of the belts in compression causes a kneading action on the fibers which results in fiber interlock and excellent compactness.

#### FIBER DISTRIBUTION AND RIBBON FORMATION - STAGE II

The newly formed lap is continuously drawn into a lickerin type intermediate opener by the action of its resilient covered feed roll in close proximity with a feed plate, Figure 3. By the action of the opener, the lap is transformed

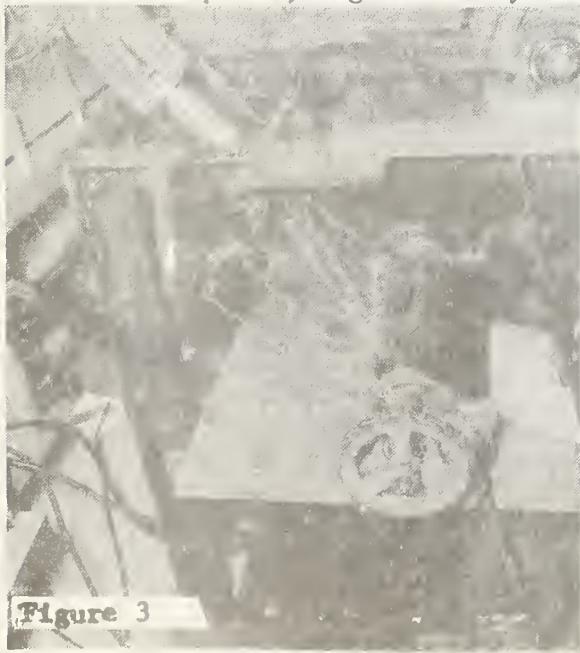


Figure 3



Figure 4

into extremely fine tufts and fibers which are subjected to a cleaning action and pneumatically doffed from the lickerin processing cylinder. The doffer, consisting of a suction nozzle incorporated into a duct, transitions from a cylinder width, narrow rectangular inlet, to a round outlet. The transitional duct is equipped with multiple adjustable louvers for maintaining an equal air velocity gradient across the duct to equally disburse the fibers into a fiber distributor. The round outlet opening serves as a journal and a pneumatic seal for a rotating entrance tube of the fiber distributor. The entrance tube is longitudinally slotted, disbursing fibers into a cylindrical chamber, wherein they are blended and sub-divided into multiple outlets. Under negative air pressure the fibers are transported from the distributor outlets through tubes to an assembly of six mini-condensers, Figure 4.

Within each condenser the fibers are separated from the airstream and collected on an inclined grid surface. The air flows through the grid openings out of each condenser into a common manifold which is connected to a filter and suction source.



A rotating take-out cylinder peripherally covered with resilient material contacts each condenser forming a pneumatic seal. The take-out cylinder rotating at constant speed in close proximity to the terminal end of the grid withdraws the fibers from the confines of the condenser, forming a continuous fibrous ribbon. A curved deflection plate serves as a guide as the ribbon is moved from the take-out cylinder to the toothed feed cylinder of a Spiral Card assembly (12,13), Figure 5.

#### FIBER INDIVIDUALIZATION AND YARN FORMATION STAGE III

The negative rake, toothed feed cylinder performs a dual function. It serves as a feeding means and as a worker roller for the Spiral Card. It is clothed with metallic card doffer wire and rotates at

117 higher rpm than the take-out cylinder to prevent accumulation of fibers in the area of ribbon transfer. The Spiral Card processing cylinder is clothed with positive rake, metallic card cylinder wire and rotates at high rpm.

To eliminate the need for suction or other type doffing means and provide positive control of the number of carding cycles, the top half of the card cover is provided with four spiral grooves. With the card cylinder rotating at self-stripping speed, the fibers are compelled by the grooves to spirally encircle the cylinder three times as they traverse the two inch width from entrance to exit. Carding action takes place between the processing and the worker cylinder; therefore, with four spirals the equivalent of four worker

rolls is attained. An exit opening is provided in the housing terminal groove to permit discharge of fibers in a low volume air stream created by the cylinder.

Individualized fibers exiting from the miniature Spiral Card are aerodynamically transported across a smooth truncated conic surface which uniformly disburses the fibers into the rotor of a unique SRRC designed OE spinner. Utilizing the "Coanda Effect" the fibers are compelled to cling to the conic surface as they are disbursed and accelerated circumferentially into the rotor.

The OE spinner rotor has within its yarn forming chamber a continuous perforated circumference located at the apex of its two mutually inclined inner surfaces, Figure 6. The peripheral holes serve as air passages. When spinning

at low rpm an outside suction source is utilized. When spinning at high rpm the air suction is generated by the rotor and no outside suction source is necessary. As the separated fibers approach and enter the spinning chamber, they are influenced by suction air velocity and centrifugal force causing fibers to straighten, de-crimp, and align themselves circumferentially. Dust and minute particles are purged from the fibers and withdrawn through the rotor air openings. Continuous air discharge through the openings appears to prevent occurrence of wax and dust collection in the yarn formation areas. Operational and preliminary testing indicate

that the SRRC OE spinner is inherently self cleaning.

Unlike most commercial OE spinners, fibers enter the rotor circumferentially through its open face on one side of the rotor, and the fibers exit as yarn through the rotor. This is made possible by means of a stationary tube within the rotor drive shaft. Yarn winding is of conventional design and can be adapted to standard yarn packaging.

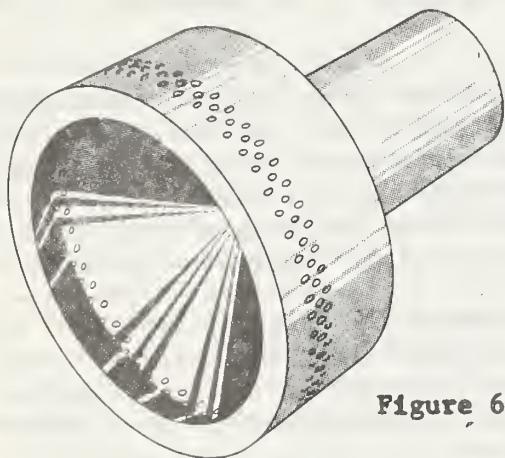


Figure 6

#### CONCLUSION

The most significant feature found within the SRRC system is its ability to efficiently subdivide and distribute fibers from a single source to multiple outputs.

Although the system is capable of producing yarn from tufts, a complete commercially acceptable concept, with an efficient number of spindle elements still lies in the future. Many of the system's problems and shortcomings, however, have been identified, and research and development work continues with the objective of continuously producing quality yarn from tufts within a single, contaminant-free machine.

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## DIELECTRIC CONSTANT OF COTTON

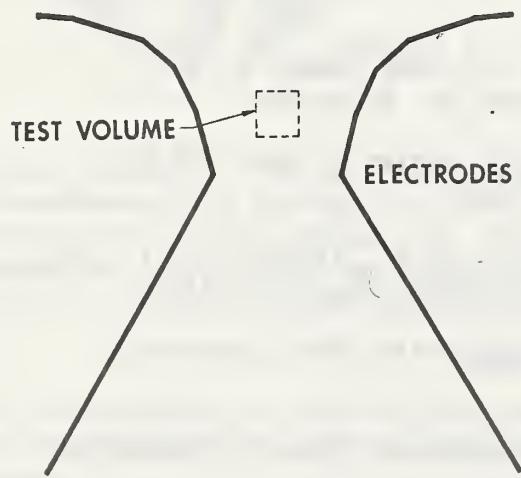
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During our research at SRRC on controlling cotton with electric fields, it was necessary to measure the effects of non-uniform fields on the motion of a cotton fiber. To evaluate this effect, it was essential that the dielectric constant or electric susceptibility of cotton be measured, since this is the determining factor.

Normally, the dielectric constant is measured by a capacitance bridge at various alternating frequencies. This technique is well developed for homogenous materials, but it is somewhat inadequate for fibrous materials; however, such measurements have been made. The capacitance measurement technique is inadequate because of the difficulty in packing the material sample uniformly.

A very simple technique was developed by Faraday and others for measuring the magnetic susceptibility of a material. The technique is based on a force measurement of a sample placed in a specially designed non-uniform magnetic field (see Fig. 1). The method is independent of the spatial

distribution of the sample. Since the field and force equations in magnetostatics and electrostatics are identical, this configuration and method should also be applicable for dielectric measurements.



$$F_x \propto V \frac{d(E^2)}{dx}$$

FIG. 1

EXPERIMENT: To make the desired electrostatic measurement, a material sample is suspended between two electrodes by a quartz fiber. Figure 1 shows the shape of the electrodes that are used and the area in which the sample is suspended. The experiment is conducted in a controlled environmental chamber using a sensitive balance to measure the initial sample

weight and the electrostatic force (see Fig. 2). When the power is turned on, the measured force is proportional to the material sample volume, the electrostatic field gradient squared, and the material electric susceptibility.

$$F = V E_0 n \frac{d(E)^2}{dx} \quad (1)$$

Where:  $F$  = Force

$V$  = Volume (sample weight/cotton density)

$E_0$  = Permittivity of free space

$n$  = Electric susceptibility

$d(E)^2/dx$  = the field gradient squared

Force measurements are made at several different voltages. The results are plotted, and the slope of the curve is a measure of the electric susceptibility since the field gradient squared is constant for a given supply voltage.

$$\frac{d(E)^2}{dx} \propto V^2 \quad (2)$$

The dielectric constant ( $k$ ) of the material sample differs from the measured electric susceptibility because empty space has a dielectric constant of unity. Therefore,

$$k = 1 + n \quad (3)$$

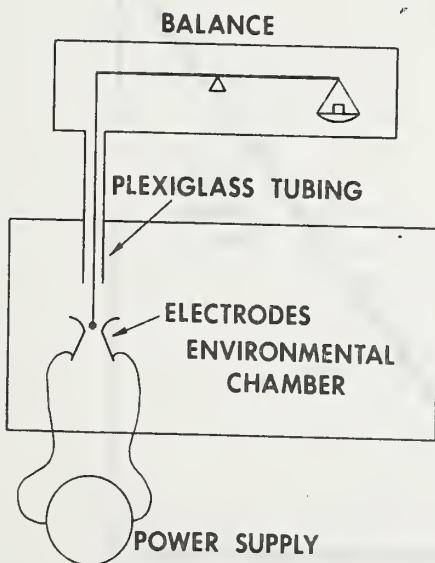


Fig. 2

The test data was taken at 60 Hz because of the available power supply and the sensitivity of the electrobalance. In addition, one of the main differences between the magnetic and electric measurement is the electric charge. With a high DC potential, the sample could accumulate a surface charge and seriously affect the force measurement.

TEST RESULTS: Most of the literature on dielectric constant measurements is for high frequency (i.e.,  $10^6$  Hz). The limited amount of data at low frequencies gives a dielectric constant for

Carnauba wax of about 7 (Fig. 3). Using several different geometries of Carnauba samples--cylinders, hollow cylinders, spheres, etc.--the results at 60 Hz varied less than 3%. With this material as a standard reference for the electrostatic field calibration, the test results indicate a dielectric constant for cotton at 60 Hz is about 17. Figure 4 is a typical curve of  $(\text{voltage})^2$  vs force. As seen, the data is quite linear and it has correlation coefficients that are consistently better than .99. These measured dielectric results appear to be high since most reports for high frequencies set the value at three to six; however, Hearle's (Reference 1) results recorded at 1000 Hz gave a value of 18.

**ANALYSIS:** To provide a check on the measured test results. A rough estimate of energy gradient  $d(E)^2/dx$  for this geometry has been made from a computer plot of the electrostatic field potential solution for direct calculation in equation 1. This method gives results of a dielectric constant for cotton of approximately 15. This value seems to be high also in view of the fact that other more compact substances like Carnauba wax, sersin wax, and quartz have values of five or six at 60 Hz; however, it agrees well with the lab tests.

Needed for the technique at this point in the research program is a calibration curve of the electric field gradient using a stable substance of well known dielectric constant.

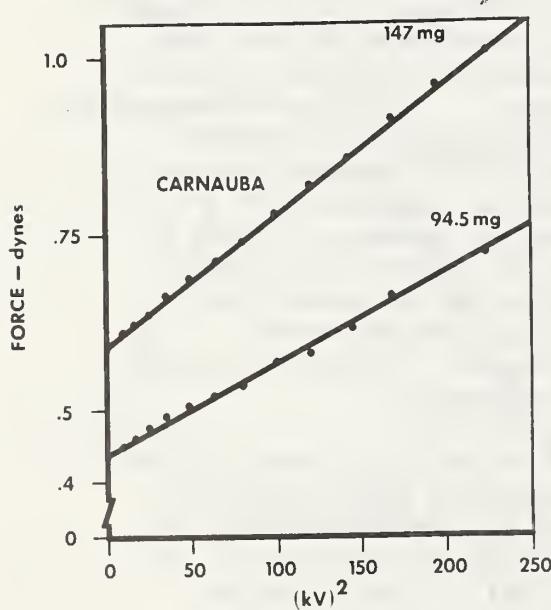


FIG. 3

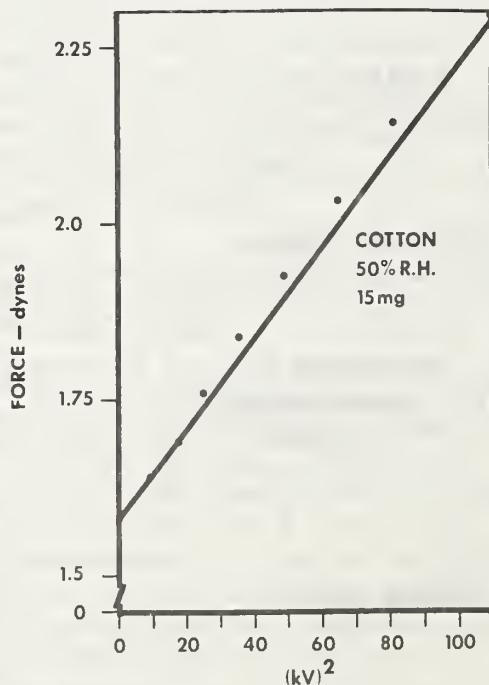


FIG. 4

CONCLUSIONS: These test results indicate that cotton has a relatively high electric susceptibility. The laboratory test and the analytical check procedure agreed quite well and both methods indicated quite high values of dielectric constant.

It is apparent that the moisture content of cotton has a strong influence on electric susceptibility. The above results were taken at room temperature (70°F) and 50% RH. Recently preliminary testing indicates a steady rise in dielectric constant with relative humidity in the range from 30% to 70% in a way that is similar to the moisture regain by the cotton. These results indicate that the high dielectric constant for cotton is a strong function of the moisture in the cotton.

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## CORONA TREATING COTTON: ITS RELATIONSHIP TO PROCESSING PERFORMANCE AND QUALITY

by

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A considerable amount of research has been devoted to studying the effects of corona treating wool and mohair fibers with both air and air/chlorine mixtures to improve the strength, shrink-proofing, and processability of these fibers (1,2,3,4,5). More recently (6,7,8) these techniques have been applied to cotton fibers with increases reported in fiber friction, yarn strength, abrasion resistance, and spinnability. Data thus far reported indicates that maximum treatment effectiveness occurs with 15 KV electrode voltage at a frequency of 2070 Hz using 95°C cell temperature, 1.4 seconds residence time, and air and chlorine flow rates of 0.35 and 0.07 scfm respectively. These conditions yielded increases in yarn strength of as much as 26% (7).

The major objective of the present research has been to evaluate a corona treatment system designed after that of Thorsen and Landwehr (5) and to determine its effect on the processing performance and quality of air-corona treated cotton card sliver. The major improvement over the original system is that it utilizes a commercial high frequency power supply designed for surface treatment of plastic films. This supply operates at a frequency of about 3300 Hz, with a continuously variable power output level up to 4.2 KVA.

### EXPERIMENTAL

Figure 1 shows a schematic diagram of the operation of the corona treater.

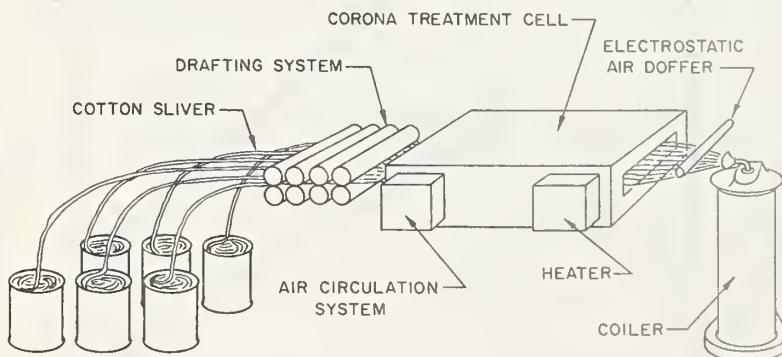


Figure 1 shows a schematic diagram of the operation of the corona treater. Six ends of 55 gr./yd. cotton card sliver are fed to a 6:1 drafting device to form a seven inch wide web. This thin web of cotton is then compressed between a Teflon coated lower wire belt and a Teflon impregnated upper fiberglass belt which convey it between the pyrex discharge electrode plates. For complete details on the corona cell construction, see the paper of Thorsen and Landwehr (5). Corona cell temperature was regulated using a Versatherm regulator with thermistor probe and Cal-Rod heating element along with internally circulated air. The cotton fiber web is then recondensed into sliver form and is fed into a conventional coiler. A combination electrostatic

air doffer is used to remove the treated fiber from the corona cell. The treated fiber is then compressed between a Teflon coated lower wire belt and a Teflon impregnated upper fiberglass belt which convey it between the pyrex discharge electrode plates. For complete details on the corona cell construction, see the paper of Thorsen and Landwehr (5). Corona cell temperature was regulated using a Versatherm regulator with thermistor probe and Cal-Rod heating element along with internally circulated air. The cotton fiber web is then recondensed into sliver form and is fed into a conventional coiler. A combination electrostatic

discharge bar and air doffer is used to remove the web from the highly charged conveyor belts.

The testing of the processing performance of corona treated cotton was carried out using a bale of 4.2 Micronaire, 1-1/16 inch staple cotton. Test lots of six pounds each of card sliver processed from this bale were treated in the corona cell at different values of cell temperature, residence time, and discharge current and voltage. The corona treatment step was assumed to be equivalent to first drawing the card sliver. Second drawing of the sliver was accomplished on the Saco-Lowell Versamatic drawframe using a 6:1 draft with six ends. The resulting sliver lots were processed into one hank roving (1.0 H.R.) on the Saco-Lowell Rovematic frame. The Belger roving tester was used to adjust the twist settings on the roving frame to obtain the same "twist hardness" for all samples. An increase in this parameter for treated roving required a decrease in the twist multiplier (T.M.). Spinning of the roving into 36/1 yarn was accomplished on an SKF Spintester which has six spindles. All of the yarn tested was spun at 12,000 rpm using three different T.M.'s including 3.7, 4.2, and 5.0. Tests on the sliver and roving included Uster uniformity (C.V.), projected mean length, fiber length, fineness, strength, and length distribution. Also included was the first drawn sliver's drafting tenacity using the West Point cohesion tester to obtain a direct measure of the intensity of corona treatment. All yarns spun were tested for Uster C.V., thick and thin spots, neps, single strand and skein break, count strength product (C.S.P.), and elongation.

## RESULTS

A mill test consisting of eight different lots was designed to include primary currents of 7 and 11 amperes, exposure times of 1.3, 3, and 6 seconds, and cell temperatures of 65 and 95°C. Two control lots were processed, one at 65°C and three seconds and the other at 95°C and 1.3 seconds. Table I summarizes these results for first drawn sliver and 1.0 hank roving.

The system used for coding these lots is that the first group of numbers refers to corona cell temperature in °C, the second group to primary treater current in amperes, and in the third group to cell residence time in seconds. Thus 95-7-1.3 refers to a treatment at 95°C with seven amperes primary current and 1.3 seconds residence time. Zero amperes current signifies no treatment applied to a control lot run through the reactor at the specified conditions. The treated lots in this table have been ordered with respect to increased tenacity of the first drawn sliver as measured with the West Point cohesion tester under controlled environmental conditions. The increased sliver drafting tenacity is accompanied by a decrease in twist hardness required for roving production. This is most evident in 95-11-6 where a reduction of roving twist of 33% results from an increased drafting tenacity of 150%. Except for the 1.0 H.R. of 95-11-6, there appears to be no deviation in Uster C.V. of the treated lots from their controls. This same trend appears in the Suter-Webb array length distribution where decreases in fiber mean length and increases in short fiber content were found in the case of 9-11-6.

TABLE I. PROPERTIES OF CORONA TREATED SLIVER AND ROVING

Lot	Drafting	Roving T.M.	Uster (%C.V.)	Projected Mean Length	Suter-Webb	
	Tenacity (gm/tex)				Mean Length (in.)	Fibers Less Than 3/8" (%)
<u>65-0-1.3</u>						
1st Drawn	.0338		4.88	.718	1.00	4.9
1.0 H.R.		1.106	6.53	.873	.97	6.4
<u>95-0-3</u>						
1st Drawn	.0348		4.84	.704	1.00	4.8
1.0 H.R.		1.106	6.30	.905	1.04	3.6
<u>95-7-1.3</u>						
1st Drawn	.0399		4.68	.711	.99	4.9
1.0 H.R.		1.022	6.48	.895	1.02	4.4
<u>95-7-3</u>						
1st Drawn	.0427		4.36	.694	.97	4.9
1.0 H.R.		1.022	6.71	.871	.96	5.8
<u>65-11-1.3</u>						
1st Drawn	.0427		4.94	.705	1.02	4.3
1.0 H.R.		1.022	6.52	.895	.97	5.9
<u>65-11-3</u>						
1st Drawn	.0492		4.40	.739	.99	6.0
1.0 H.R.		0.985	6.50	.889	.98	6.0
<u>95-11-3</u>						
1st Drawn	.0629		4.52	.710	.99	5.6
1.0 H.R.		0.919	6.69	.876	.95	6.6
<u>95-11-6</u>						
1st Drawn	.0872		4.64	.498	.92	8.8
1.0 H.R.		0.740	7.20	.654	.86	8.5

Data on properties of yarns spun from these lots are shown in Table II. Corona treated lots show an increase in the single strand C.S.P. over the controls in 15 of the 18 cases. For each of the six treated lots, the value of percent increase of C.S.P. over the corresponding control varies inversely with the twist multiplier. The maximum in single strand C.S.P. (16.4%) was for 65-11-1.3, also at 3.7 T.M. Similar results were observed for tests of the skein break C.S.P. for the same lots. These results were surprising in that lots 95-11-6 and 95-11-3 showed the highest sliver tenacities after treatment (See Table I). This was totally unsuspected in light of Thorsen's findings (7).

TABLE II. PROPERTIES OF YARN SPUN FROM CORONA TREATED COTTON

LOT	% C.V. (USTER)	SINGLE STRAND BREAK			SKEIN BREAK		
		C.S.P.	% INCREASE	% C.V.	C.S.P.	% INCREASE	% C.V.
<u>65-0-1.3</u>							
3.7 T.M.	19.85	250	-	11.63	1970	-	5.87
4.2 T.M.	19.74	265	-	11.66	2126	-	3.99
5.0 T.M.	19.96	290	-	10.36	2161	-	4.04
<u>95-0-3</u>							
3.7 T.M.	19.81	250	-	11.87	2099	-	3.86
4.2 T.M.	20.03	274	-	11.32	2170	-	3.82
5.0 T.M.	20.00	287	-	11.85	2242	-	3.57
<u>95-7-1.3</u>							
3.7 T.M.	20.32	273	9.2	11.38	2160	2.91	3.88
4.2 T.M.	20.39	277	1.1	11.43	2188	0.83	3.67
5.0 T.M.	20.85	282	-1.8	11.88	2130	-4.99	6.07
<u>95-7-3</u>							
3.7 T.M.	20.32	263	5.2	10.88	1978	-5.76	10.21
4.2 T.M.	20.60	264	-3.8	13.83	2056	-5.25	11.18
5.0 T.M.	20.17	276	-3.9	15.73	2082	-7.14	8.84
<u>65-11-1.3</u>							
3.7 T.M.	19.89	291	16.4	10.39	2182	10.76	4.22
4.2 T.M.	20.03	293	10.6	11.19	2250	5.83	3.80
5.0 T.M.	20.38	305	5.2	10.34	2253	5.97	3.03
<u>65-11-3</u>							
3.7 T.M.	20.58	305	22.0	10.32	2216	12.5	3.26
4.2 T.M.	20.47	297	12.1	10.07	2242	5.46	4.03
5.0 T.M.	20.59	307	5.9	11.04	2245	3.89	3.93
<u>95-11-3</u>							
3.7 T.M.	21.12	271	8.4	12.87	2022	-3.67	11.05
4.2 T.M.	21.18	282	2.9	14.86	2115	-7.14	10.29
5.0 T.M.	21.13	287	0.0	18.78	2018	-9.99	11.12
<u>95-11-6</u>							
3.7 T.M.	24.26	277	10.8	13.70	2014	-4.05	5.41
4.2 T.M.	24.56	289	9.1	15.46	2156	-0.65	5.45
5.0 T.M.	24.29	301	3.8	17.94	2066	-7.85	5.78

## CONCLUSIONS

The most significant finding of this research has been that an approximate 50% increase in frequency of corona discharge has lowered the cell temperature requirements for optimum treatment from 95°C to 65°C. This research has

also characterized the detrimental effects on cotton yarn processing parameters caused by over-treating sliver with corona discharge. Finally, it has been shown that yarns spun from corona treated cotton could be produced with significantly lower twists than feasible with untreated cotton, with higher or equal strength than control yarns with higher twist.

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## SELECTED PHYSICAL AND CHEMICAL METHODS FOR THE ANALYSIS OF COTTON/POLYESTER BLENDS

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### INTRODUCTION

In research work with yarns and fabrics containing various mixtures of cotton and polyester, it is necessary to know the percentages of each fiber component. Furthermore, in the labeling and sale of blended fabrics and textile products, it is necessary to know the composition within 3%. This is so stated by rule 43A, from the rules and regulations under the Textile Fiber Products Identification Act of 1960 of the Federal Trade Commission<sup>1</sup>.

Both destructive and nondestructive methods for the analysis of cotton and polyester blends will be discussed. In the destructive methods the cotton component can be removed by (1) cold 70% sulfuric acid or by (2) hot sodium hypochlorite solution. The polyester can be removed by (3) degradation with 45% sodium hydroxide, (4) monoethanol-amine or (5) tetrachloroethane in the presence of either sodium bicarbonate or sodium acetate.

The nondestructive quantitative methods of analysis involve (1) moisture regain and (2) density. The qualitative method (3) is by selective staining.

### EXPERIMENTAL AND RESULTS

The first destructive method is the AATCC sulfuric acid method<sup>2</sup>. A weighed sample of cotton/polyester is immersed in boiling 1% sulfuric acid for approximately 10 minutes. Next it is transferred to a fritted glass funnel where a vacuum is applied to remove the excess acid solution. After cooling, the sample is put into 70% sulfuric acid at 38°C and stirred for 15 minutes. The acid solution and remaining fibers are poured cautiously and quickly into cold water. After filtering the fibers from the solution, they are washed with water, neutralized in an alkaline solution of sodium bicarbonate, washed with water again, and dried and weighed. Test results of the sulfuric acid method are accurate and reproducible within  $\pm 1.0\%$ <sup>3</sup>.

The second destructive method used at SRRC is the sodium hypochlorite (Clorox) procedure<sup>4,5</sup>.

A weighed sample of cotton/polyester is put into a Gooch Crucible that has a fixed perforated porcelain bottom and removable perforated porcelain disk top. About 100 ml of preheated Clorox at 88°C is used

per gram of dry sample. The crucible with sample is placed in the Clorox, and the reaction is allowed to proceed for 10 minutes or until the Clorox loses color. The treatment is repeated at least three times with new hot Clorox. Samples are then washed with water, 2.5% sodium bisulfite and finally with water again and dried. The percentage of polyester in the blend is calculated from the dry weights before and after treatment.

To show that the two burn-out methods are equivalent, a comparison of the Clorox and sulfuric acid methods is shown in Table I.

A statistical comparison of the methods which shows that the differences are not significant at the 95% level has been published recently in the Textile Chemist and Colorist<sup>6</sup>.

Because the sulfuric acid and Clorox methods give equivalent results, and because the Clorox method is more convenient and less dangerous, results from the latter method will be used as a basis of comparison for all other analyses mentioned, both destructive and nondestructive.

The third destructive method used to analyze for the polyester in a cotton/polyester blend is the sodium hydroxide procedure<sup>6</sup>. A weighed sample of cotton/polyester blend in the Gooch Crucible is immersed and agitated for 1 hour at 100°C in 100 ml per gram of 45% sodium hydroxide. During this process the polyester is converted to ethylene glycol and a salt of terephthalic acid. The remaining cotton is washed with water, 5% acetic acid, and again with water. After drying, the percentage of cotton in the blend is calculated from the dry weights before and after treatment. A small correction factor, based on the weight loss for 100% cotton is used because of the slight degradation of cellulose in the 45% sodium hydroxide.

The percentages of polyester by the Clorox method and by the sodium hydroxide method after correction for a 2.3% loss of cellulose are shown in Table II. Differences show that from the three sets of samples, i.e., fiber, woven blends from the same cotton and polyester, and knit goods from a different source of cotton and polyester, all analytical results are within  $\pm$  3% of the values as determined by the Clorox procedure.

The fourth destructive method is the dissolution of polyester in boiling monoethanolamine. A weighed sample of cotton/polyester blend is immersed in 100 ml of monoethanolamine per gram, and the mixture heated to reflux (171°C) for 15 minutes. After cooling, the residue is removed, collected in a Gooch Crucible, washed with distilled water, then with 5% acetic acid, and again with water. The residue is then dried and weighed.

As with the sodium hydroxide method, a correction factor is needed. This factor is based on the weight loss when 100% cotton is put through the process. Although many laboratories will want to establish their own correction factor for each material used, an average 2.4% factor was used in this work. The percentage of cotton in a blend is calculated from the dry weights before and after treatment. Results for a range

of blend compositions obtained with the monoethanolamine procedure are compared with results obtained with the sodium hypochlorite method as shown in Table III. In every case the results were within  $\pm 3\%$ .

The fifth destructive method is the use of hot tetrachloroethane, a solvent for polyester, to extract polyester from cotton/polyester blends. The cotton remaining is often severely damaged, presumably because of in situ generation of hydrogen chloride from tetrachloroethane and moisture in the cotton. Much of the damage can be prevented by treating the blend with a saturated solution of sodium bicarbonate or 10% sodium acetate. In either case the weighed blend is treated with a solution of the basic salt and dried in an oven at 110°C. The treated blend is immersed in 20 ml tetrachloroethane per gram and the combination heated to reflux (147°C). The mixture is then cooled to room temperature in an ice bath. The blend residue is transferred to fresh tetrachloroethane and the heating-cooling process repeated two more times. The remaining cotton is washed three times with ethanol, and then three times with water. The residue is dried for 1/2 hour at 110°C.

In comparing the percent of cotton found by tetrachloroethane and the two basic salts used (sodium bicarbonate and sodium acetate) with the Clorox method, the differences indicated in Table IV show that from two sets of samples, i.e., woven blends and knit goods from a different source of cotton and polyester, all analytical results are within  $\pm 3\%$  of the value as determined by the Clorox procedure.

On the nondestructive side, a moisture regain and a density method serve as quantitative methods while selective staining serves as a qualitative method for analyses of blended yarns and fabrics.

Moisture regain values have been obtained in duplicate under standard conditions for eleven cottons and cotton/polyester blends. A calibration plot of percent cotton (Clorox method) versus moisture regain (R) was made as shown in Figure 1, and the least squares line was calculated. The correlation coefficient is 0.997. The equation for this line (% cotton = 15.2R - 2.11) can be used to calculate the composition of unknown blends after moisture regain values have been obtained.

The density method is the second nondestructive physical method for analysis of blended yarns and fabrics. If a piece of cotton ( $d = 1.54$ ) is placed in carbon tetrachloride ( $d^{25} = 1.59$ ), it floats. If heptane ( $d^{25} = 0.68$ ) is added slowly to the carbon tetrachloride, a point is reached where the cotton neither floats nor sinks. As more heptane is added, the cotton sinks. Similar results are obtained if polyester ( $d = 1.40$ ) or a polyester blend is used in place of cotton. Theoretically it should be possible to prepare a calibration curve relating percentage of polyester in blends of known composition to the ml of heptane (B value) which must be added in each case to 100 ml of carbon tetrachloride to cause a no float/no sink condition. Because of the time required to reach equilibrium after each addition of heptane, the process is too slow to be practical. In actual practice the

calibration curve was prepared in the following manner: To each of 25 bottles labeled B=4 through B=28 were added 100 ml of carbon tetrachloride and then the corresponding B ml of heptane.

Six desized, scoured, and bleached fabrics which had been made at SRRC from cotton or cotton and Kodel 421 polyester with known polyester content were used for density measurements. In addition a sample of Kodel 421 polyester fabric obtained by removing cotton from one of the blends with hot Clorox was also used. The samples were cut into 1.5 cm<sup>2</sup> pieces, oven dried, and conditioned in a conditioning room overnight. The moisture regain was negligible for the polyester and 7% for the cotton. The samples were placed in the labeled density bottles in the conditioning room. The bottles were then capped and removed to the water bath in the laboratory at 25  $\pm$  0.2°C. The next day the B values were determined to B  $\pm$  0.5 by one of two methods.

In Method I (left side of bath in Figure 2), the sample and one of the prepared liquids have the same density. A no float/no sink situation occurs in that bottle, and the B value is read directly from that bottle. In all bottles with a lower B value the sample will float; in all bottles with a higher B value, the sample will sink.

In Method II (right side of bath in Figure 2), no bottle contains a liquid with a density the same as the sample. The sample will float in all bottles where the B value is too low, and sink in all bottles where the B value is too high. The true B value lies somewhere between the bottle in which the sample last floats and first sinks. If it is assumed to be exactly half-way between, the B value will be accurate within half a unit.

A plot of percent polyester versus B values is shown in Figure 3. The least squares line which can be used to calculate the composition of the cotton/polyester blend is also given.

Several knit (cotton/Fortrel) and woven (cotton/Kodel) blends have been analyzed qualitatively to determine their approximate composition by selective staining. All of the samples were stained with T. I. S. identification stain No. 2 (Test Fabrics, Inc.). This stain colors cotton blue and the polyesters used in this work yellow. After staining, it is a simple matter to look at the blends and arrange them in order as the color changes from blue to yellow with decreasing cotton-content, as shown in Table V.

This test can also be used to confirm complete removal of cotton or polyester from a blend that has been analyzed by one of the destructive methods discussed earlier. In addition it can be used to stain blends that are to be used as standards in the density method.

#### CONCLUSIONS

Three of the five destructive methods are straightforward in that they do not require a correction factor. The authors prefer the Clorox

method because it is probably the simplest and safest of these methods. Of the two methods that do require a correction factor the authors recommend the sodium hydroxide procedure because the reagents are easily available and pollution problems are minor. The regain and density methods, while good, require a conditioning room and time for the samples to reach equilibrium. Once the density method is in operation, it has an advantage over the other methods discussed because technical operations are at a minimum. The staining technique although qualitative is easy and is the fastest of all the methods.

The authors thank Myles A. Patureau for furnishing the sliver, Dorothy C. Legendre for running analyses by the sulfuric acid method, and John D. Tallant for statistical calculations.

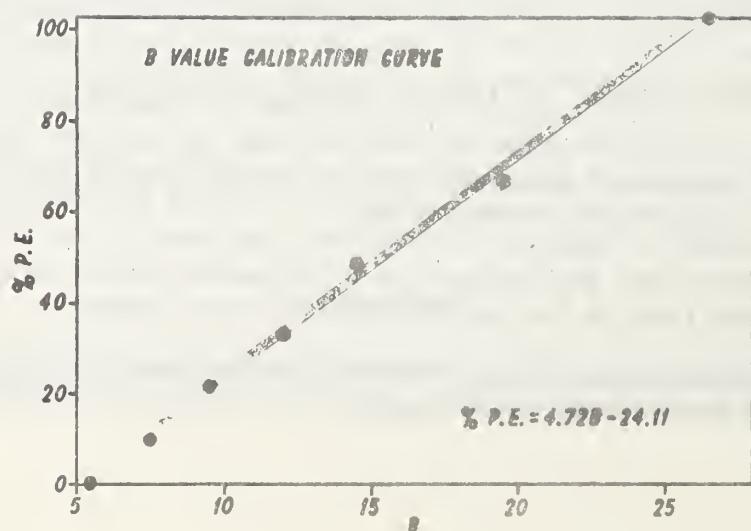
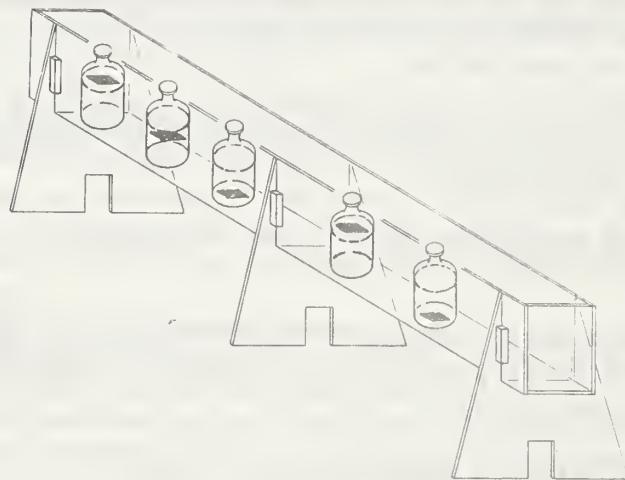
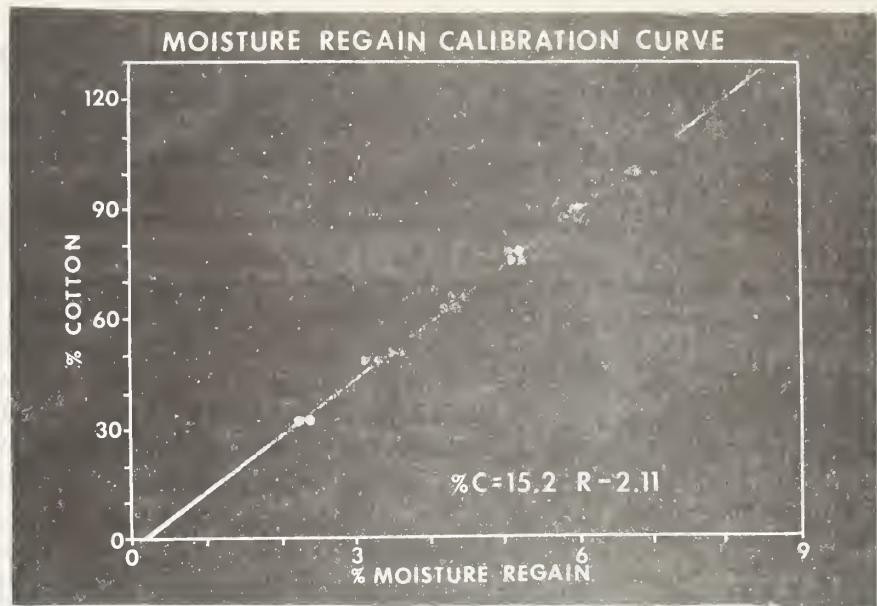
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Figure 1. Relationship Between Moisture Regain and Cotton Content of Cotton/Polyester Blends.

Figure 2. Sink/Float Situations for a Cotton/Polyester Blend in Solutions of Carbon Tetrachloride and Heptane.

Figure 3. Relationship Between the B Value and the Polyester Content of Cotton/Polyester Blends.



## COTTON CLOTHING ATTRIBUTES IN SUBJECTIVE COMFORT\*

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## INTRODUCTION

The role of clothing in dealing with comfort involves the three-way interaction of clothing, body response and environment. Appearance and fit are important for peer acceptance leading to comfort. Psychological response to clothing can be dominant in many wearing circumstances, particularly as influenced by clothing contact sensations. Fabric surface differences as they affect skin contact can therefore be very important and these effects in cotton clothing form the main focus of this presentation.

## CLOTHING CONTACT COMFORT METHODS

Figure 1 shows a convenient laboratory arrangement for carrying out clothing comfort tests on people. The dressing room if heated can serve as an exercise room to produce sweating and provide an easily repeated metabolic starting condition for clothing tests. Microclimate control in the environmental chamber is essential for generating, in a repeatable fashion, the clothing contact sensations.

The most effective techniques for making clothing comparisons were developed using all cotton shirts on subjects who were made to sweat and subsequently sat in the test chamber at 95°F. Figure 2 shows how water collected in a particular shirt varied as a function of the water content of the air or relative humidity of the chamber. As the test proceeded, the subjects were asked to give a subjective response to their comfort condition using a simple scale of 1 - totally uncomfortable to 5 - completely comfortable. Figure 2 shows that the subjective comfort ratings (SCR) given were also a function of relative humidity of the air and the water content of the shirt.

As tests on different shirts continued it became clear that consistent SCR ratings were much easier to obtain if associated with a particular comfort sensation. Thus, as shown in Figure 3, clothing comfort levels were assessed by giving comfort ratings for each sensation noted, and subjects were encouraged to use descriptors they preferred in describing their comfort condition.

Figure 4 shows the results of such tests on print cloth shirts having four levels of resin add-on. Obviously some comfort sensations were stimulated by resin content more than others but, as summarized in Figure 5, the main concern in producing these sensations on cotton shirts would come with the high add-ons of some flame retardant finishes.

Operating on the premise that shirtings with a fuzzy surface, and hence less direct skin contact, would generally be more comfortable than their smooth counterparts, the interaction of resin level and fabric surface was studied as shown in Figure 6. The oxford shirt, worn in a chamber at 95°F and high water

\* Work supported in part by the Southern Regional Research Center, U.S.D.A. and in part by Cotton, Incorporated

vapor pressure, was reasonably comfortable. With resin alone added, loss of comfort was evident in sensations of snug, sticky, damp, and clingy. Napping of the resin treated fabric surface restored the shirt to a fairly comfortable condition in terms of these same four comfort descriptors. This work taught, therefore, that high temperature combined with high humidity were important conditions to include in comparing the comfort properties of shirts and, in addition, the surface fuzziness or smoothness was important in assigning the causes of comfort differences of worn shirts.

Multiple tests of woven and knit shirts were carried out using this same approach to comfort testing. Within each shirt series considerable effort was expended in achieving shirtings of comparable surface smoothness. Subjects were made to sweat by exercising in a warm room and then exposed while seated to 95°F at 25% R.H., shifting to 70° R.H. and then to 60°F and 60° R.H. A typical set of subjective comfort curves for three woven shirts on a single subject are shown in Figure 7. The lowest comfort ratings on each shirt occurred when the temperature and relative humidity were both high and returned to normal comfort levels when there ceased to be sweat at the skin clothing interface. Duplicate tests were made with each shirt on each subject. At no time was the subject informed as to which shirt he was wearing.

#### RESULTS OF SHIRT COMPARISONS

The woven shirts, two with 100% cotton (COWC and C100) and two cotton/polyester blends (C67C and C33C) were compared on 100 subjects using the protocol just described. Based on the comfort ratings for each descriptor, the shirts were ranked 1st, 2nd, 3rd or 4th, and the results for the descriptor "sticky" are given in Figure 8. Either all-cotton shirt was ranked most often 1st, the blend with 67% cotton most often 3rd, and the blend with 33% cotton either 3rd or 4th. As Figure 9 shows, even the average ratings for comfort descriptor "clingy" gave a similar separation between the all cotton shirts and the two blends. Note also, the lowest comfort ratings occurred at 30 minutes when the microclimate reached 70% relative humidity at 95°F. The average comfort rating data were used in an analysis of variance for each comfort descriptor with the results shown in Figure 10. This analysis confirmed that the cottons were indistinguishable from each other in comfort rating but more comfortable than either blend at the 99% confidence level.

The knit shirts, two with 100% cotton (K100 and KFRC), one with 50% cotton (K50C), and one all polyester shirt (KAPE), were compared on 25 subjects using a very similar test protocol. The ranking results are shown in Figure 11. The flame retardant treated cotton (KFRC) was found to behave surprisingly similarly to the control (K100) with shrink resistant treatment only, and ranked first about equally often. The 50/50 blend ranked third and the all polyester shirt fourth. Analysis of variance was again applied to the comfort data with results as shown in Figure 12. The clear separation of the response to these shirts using only 25 subjects is partially attributed to the fact that knits conform to and therefore touch the body at more locations and partially to the fact that no undershirt was worn in the knit shirt study.

Combining the conclusions from the two shirt comfort studies the work supports that under conditions of mild sweating the cotton shirts, woven or knit, are clearly sensed as being more comfortable than the blends or all polyester at a high confidence level. Indeed, among the possible factors which could explain these observations, the rapid removal of sweat from the clothing-skin interface achieved by the cotton garments appears to be the most likely mechanism.

Figure 1  
COMFORT TESTING FACILITY

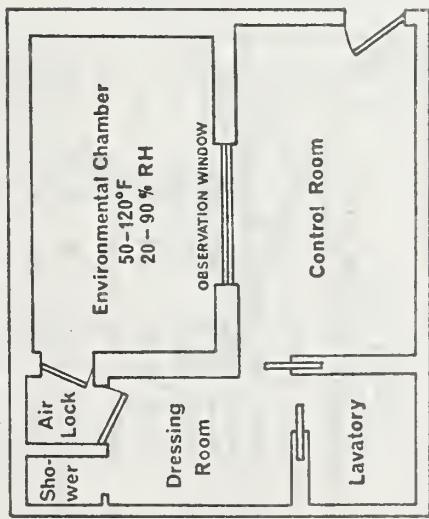


Figure 3  
SUBJECTIVE COMFORT RATING CHART

Comfort Descriptor	0	15	30	45	60	75
Stiff	-	-	-	-	-	-
Staticy	-	-	-	-	-	-
Sticky	-	-	-	-	-	-
Non-absorbent	-	-	-	-	-	-
Cold	-	-	-	-	-	-
Clammy	-	-	-	-	-	-
Damp	-	-	-	-	-	-
Clingy	-	-	-	-	-	-

Comfort Intensity Scale

1      2      3      4      5

Totally  
Uncomfortable      Completely  
Comfortable

Figure 4  
SPECIFIC SUBJECTIVE COMFORT RATINGS

PRINT CLOTH SHIRT, 95°F, WATER VAPOR PRESSURE 20 mm of Hg	Resin Added (%)	0	6	12	18
Clingy	5	2	2	2	
Picky	5	4	3	2	
Sticky	5	5	2	2	
Scratchy	5	5	5	2	

Figure 5  
CHEMICALLY FINISHED COTTON FABRICS

CLASS	ADD-ON (%)	PURPOSE
SOFTENERS	1-2	Acceptable skin contact, conformation to body
CROSSLINKERS	3-12	Smooth drying, easy care, non-wrinkling while worn
FIRE RETARDANTS	5-30	Flame resistance, flame proofing
REPELLENTS	1-5	Quick drying, waterproofing, non-staining by oils

Figure 6  
SPECIFIC SUBJECTIVE COMFORT RATINGS

		OXFORD SHIRTS, 90°F, WATER VAPOR PRESSURE 25 mm of Hg	
Resin Added	No	Yes	Yes
Surface Napped	No	No	Yes
Snug	4	2	4
Sticky	4	2	4
Damp	5	2	5
Clingy	5	2	5

Figure 7

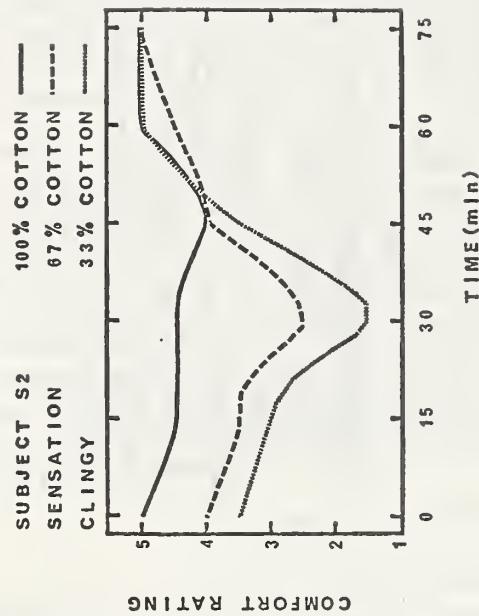


Figure 12

COMPARISONS BETWEEN SHIRTS  
FROM COMFORT RATING AVERAGES

Analysis of Variance 0-45 Min

Comfort Degrees Rating Diff. Shirts Diff. Sign.  
Comment Freedom CGW66 C1896 B6396 at 99%

Comfort	Degrees	Rating	Diff.	Shirts	Diff.	Sign.	
Comment	Freedom	CGW66	C1896	B6396	K1006	K2006	
Sticky	2335	0.09	0.57	0.27	0.10		
Damp	1919	0.01	0.73	0.21	0.11		
Clingy	2079	0.10	0.70	0.32	0.11		
Glammy	703	-0.08	0.65	0.49	0.20		
Non-Abs.	959	0.19	0.54	0.32	0.16		
						at 99%	
Sticky			380	0.00	0.60	0.50	0.21
Damp			412	0.05	0.60	0.41	0.19
Clingy			508	0.04	0.57	0.64	0.18
Glammy			124	0.28	0.91	0.63	0.39
Non-Abs.			284	0.54	0.38	0.57	0.26

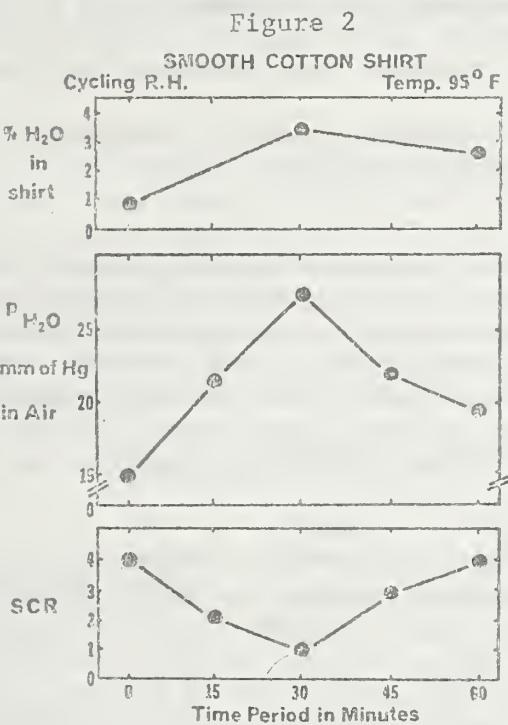


Figure 9  
AVERAGE COMFORT RATINGS  
COMMENT CLINGY

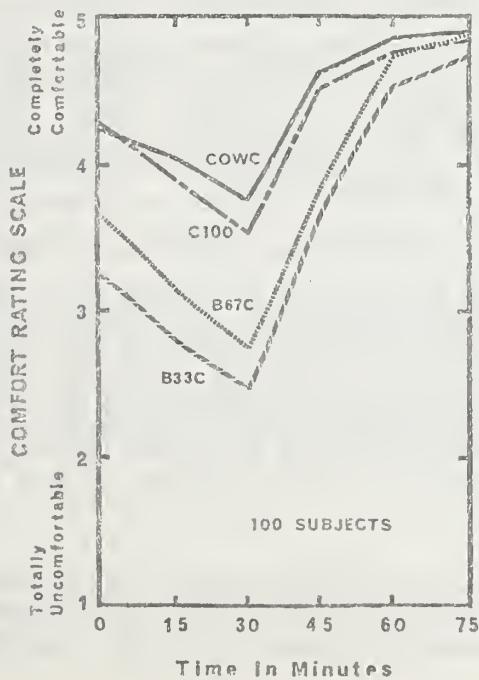


Figure 8  
SHIRT PREFERENCE FROM RANK POSITION  
AT 15 AND 30 MINUTES  
100 SUBJECTS COMFORT COMMENT: STICKY

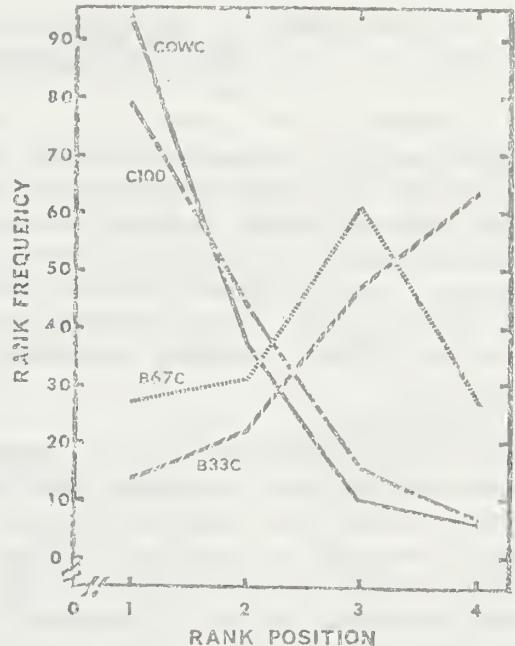
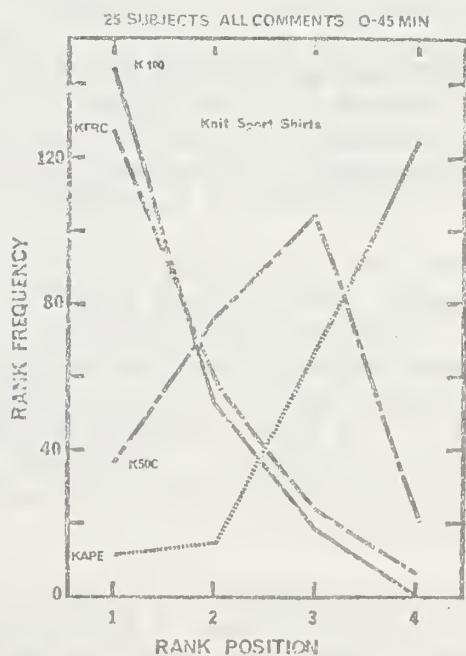


Figure 11  
SHIRT PREFERENCE FROM RANK POSITION



A STUDY OF THE EFFECT OF LIQUID AMMONIA ON  
COTTON'S PHYSICAL PROPERTIES AND YARN PROCESSING

by

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As part of an extensive research program to reduce processing cost and improve yarn quality, an investigation is being conducted to chemically alter those properties of cotton fibers which influence processing efficiency. Comprehensive investigations of fiber additives and their effects on processing, dyeing, and finishing of yarn or fabric have not been reported. The objective in treating fiber was to not only alter fiber physical properties but improve carding performance, reduce twist requirements, and improve dyeability.

Even though commercial liquid ammonia treatments such as Prograde are generally applied to cotton yarn or fabric, research on applications to cotton fibers has shown increased fiber cross-sections and elongation (1). Liquid ammonia is inexpensive, has a low boiling point, and is able to swell cotton fibers rapidly while increasing the fiber affinity for dyes. It may have potential use as a treatment to improve processing of low Micronaire or immature fine fiber. Ambient temperature should suffice for evaporation of the ammonia, and an enclosed cyclic system could be used for fiber treatment. The tendency of liquid ammonia to dissolve the outer layers of fats, waxes, and pectins as occurs during caustic mercerization of cotton fiber should be less of a factor, but higher fiber friction could hinder carding.

Processing Measurements and Test Methods: Fiber length, strength, elongation, and fineness were determined by ASTM procedures on cotton samples taken from liquid ammonia treated lap and finisher drawing sliver (2). Fiber resiliency was determined in an experimental device. The compressed and recovered heights were used as a measure of fiber resiliency (3).

Cardability was gauged by measuring fiber load in the card, waste, and neps. Neps were counted after sampling the card web during operation using the North Carolina State technique. Fiber parallelization was determined from selected sliver samples after the second process of drawing by the Projected Mean Length method. Fiber cohesion or drafting tenacity was made on rovings using a West Point Cohesion Tester (4). Interfibrillar swelling and the percentage of Cellulose I of native cellulose remaining was measured as a crystallinity index using X-ray diffraction analysis of test samples of lap and rovings (5).

Five Second Immersion: Breaker picker laps were made using a four-bale blend of 1-3/32 inch, 3.0 Micronaire, Middling Light Spot. Each of the laps was split into five equal widths and encased in cheese cloth to support the

laps during the liquid ammonia padding and drying. The split laps were padded in liquid ammonia for five seconds and dried at ambient temperature and humidity for 24 hours in a lab hood. The dried laps were broken apart by hand and processed into finisher picker laps.

The crystallinity index is a measure for determining the treatment effectiveness. Only a small reduction in the crystallinity index for Cellulose I occurred. The crystallinity index of the untreated lap is 86%, and the five-second treated lap had 82% Cellulose I remaining. The increased swelling found in ammonia-treated roving is indicated by a further reduction in the crystallinity index to 77% for treated roving fiber. The effect of the liquid ammonia on lap fiber properties is shown in Table I. An increase in fiber cross-section or Micronaire, elongation, and resiliency with accompanying decreases in fiber length and tenacity occurred.

TABLE I. EFFECT OF LIQUID AMMONIA ON FIBER PROPERTIES

TREATMENT <sup>1/</sup>	MICRO-NAIRE	MEAN LENGTH (in.)	TENACITY (gm/tex)		ELON- GATION (%)	RESILIENCY	
			0-GA.	1/8-GA.		COMPRESSION (in.)	RECOVERY (in.)
Untreated	3.0	0.96	38.9	23.0	7.4	2.7	3.0
5 seconds	3.4	0.91	38.1	20.8	8.5	3.0	3.4
30 seconds	3.5	2/ <sup>2/</sup>	39.2	21.7	9.9	3.2	3.8

1/ Time of lap immersion in liquid ammonia.

2/ Fiber entanglement caused breakage in testing.

Microscopic examination showed that the ammonia treated fibers were more swollen than the untreated fibers. There were clusters of a deposit on the surface of the ammonia treated fibers. These clusters were not present on the untreated cotton fibers. The clusters are believed to be wax dissolved by the liquid ammonia and redeposited on evaporation of the ammonia. This was the first indication of an adverse effect of the liquid ammonia. Increased fiber friction due to poor distribution of natural waxes could cause excessive card loading. This could offset any processing advantages due to increased Micronaire, elongation, and resiliency.

Table II shows the results of pertinent data from tests made on carded cotton. Carding of the ammonia-treated cotton and control was done at 30 pounds per hour, producing 55 grains per yard sliver on a metallic wire card. There was increased nepping, card load, weight per flat strip, evenness C.V., and a reduction in the fiber projected mean length.

TABLE II. CARDED QUALITY

TREATMENT	NEPS/GR.	CARD LOAD <sup>1/</sup> (gr.)	FLAT STRIP WT. (gr.)	EVENNESS (%)	LENTH	PROJECTED MEAN LENGTH <sup>2/</sup> (in.)
Untreated	5.9	945	14.0	3.9	0.65	0.52
5 seconds	13.4	1106	17.5	4.0	0.6	0.50

1/ Fiber on cylinder and flats.2/ A measure of fiber parallelization in the sliver.

Table III compares the drafting tenacities of the ammonia-treated cotton and the untreated control. The greater drafting tenacities of the treated rovings could be due to a partial removal and reposition of wax on the fiber. The percentage of Cellulose I remaining in the ammonia-treated roving was 77% compared to 87% for the control roving. The 7% Cellulose I in treated fiber from roving indicates a continued reaction between residual ammonia and cellulose, as the treated lap had 82% Cellulose I remaining.

TABLE III. EFFECTS OF IMMERSION TIME

TREATMENT	CRYSTALLINITY <sup>1/</sup> INDEX (%)		DRAFTING TENACITY (mgm/tex)
	LAP	ROVING	
Untreated	86	87	21.5
5 seconds	82	77	24.3
30 seconds	66	67	23.0

1/ Index of native cellulose.2/ 1.47 turns per inch, 1.33 hank.

Table IV shows that the untreated control yarns were superior to yarns made from the ammonia-treated cotton in all respects except elongation and grade. The twist required for maximum strength was the same for the ammonia treated and control yarns. Minimum ends down for the treated and untreated occurred with a 3.5 twist multiplier. The minimum ends down for the control was 7, whereas the ammonia treated had 31.

TABLE IV. YARN DATA, 24/1

TREATMENT	TWIST MULTI- PLIER	CSP		ELON- GATION <sup>1/</sup> %	EVEN- NESS <sup>1/</sup> %	IPI <sup>1/</sup> (neos)	YARN GRADE
		SKEIN (lbs.)	SINGLE STRAND, gm.				
Untreated	3.5	2032	250	7.5	19.2	233	D
	4.3	2096	282	8.2	19.1	230	D
5 seconds	3.5	1730	227	8.0	22.3	549	D
	4.3	1820	246	8.4	22.2	613	D

1/ Uster measurements

The 24/1 yarn, made from treated fiber, was routinely knit on a ribber. The fabric shrinkage, weight, and dyeability of the untreated and treated fabrics were for all practical purposes identical. Burst strength of the bleached knit was reduced 11% by the ammonia treatment of the fiber.

Thirty Second Immersion: To attain a more marked change in Micronaire and crystalline structure, the lap immersion time in liquid ammonia was increased. Untreated split laps of the same 3.0 Micronaire cotton were immersed in liquid ammonia for 30 seconds. Drying time was reduced from 24 hours to 4 hours. These time changes could also aid in dispersing the wax clusters or prevent their formation.

Two other lots of the cotton were immersed in liquid ammonia for 30 seconds. A soluble methoxylated polyethylene glycol was used in solution with the ammonia to yield 6% and 1% add-ons. Use of this lubricant was an attempt to aid in recoating the fiber by deposition during evaporation.

The treated laps were unrolled on wooden racks outdoors for evaporation of the ammonia. It was a clear sunny day with the temperature at about 65° F and 55% relative humidity.

Table I contains the pertinent fiber data of samples taken from 30 second ammonia treated laps. The Micronaire, elongation, and resiliency were increased. The increase in Micronaire and elongation indicates greater fiber swelling due to the longer ammonia treatment time.

It was noticed that immediately after exposure to the air during the unrolling of the treated wet laps, the liquid ammonia vaporized rapidly. Microscopic examination showed the fiber ruptured by some sort of internal explosion. No ruptured fibers were noticed in untreated cotton. This adds additional evidence to the hypothesis that fiber rupture may have occurred because of the rapid expansion of the liquid ammonia into gaseous ammonia within the cotton fiber.

Cross-sections of lap and roving fiber of untreated, 5-second, and 30-second lap treatments showed that there is increased swelling and rounding of the fibers in both lap and roving due to the 30-second immersion. The crystallinity index of 30-second ammonia treated lap was 66% remaining Cellulose I compared to 82% for the 5-second treatment. The 30-second treatment gave smoother fiber surfaces with fewer and smaller wax clusters.

All of the 30-second treated laps contracted or shrank markedly in width due to the ammonia treatment. Visual examination showed that the 30-second treated laps contained more tight neps than untreated or 5-second ammonia treated laps. Nep potential or degree of fiber entanglement was much higher with the longer treatment time due to this swelling action.

The 30-second treated laps, even those with added lubricant, carded at 30 lbs. per hour for only a short period of time before card loading increased to the

point that web quality was unacceptable. Sufficient sliver was processed to obtain crystallinity and roving drafting tenacities shown in Table III. The effect of treatment time on lap and roving crystalline structure is clear. The crystallinity index of both roving and lap is decreased as immersion time in ammonia increases. The crystallinity index of roving fiber was reduced from 87% to 77% with 5-second treatment and 67% with 30-second treatment. Drafting tenacity was again higher than the control.

Conclusions: (1) Immersion time and Micronaire (fiber cross-section) are directly related. (2) Micronaire, fiber resiliency and elongation, and drafting tenacity are increased by treatment with liquid ammonia (3) Rapid evaporation of liquid ammonia from saturated cotton ruptures fiber. (4) Increased fiber entanglement due to swelling of laps during treatment, removal and redeposition of natural waxes, and fiber damage from rapid evaporation of the ammonia were more important in carding than increased Micronaire and elongation. (5) Increased drafting tenacity did not reduce roving twist requirements of improve fiber parallelization.

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## THERMOMECHANICAL PROPERTIES OF TEXTILES: STUDY OF TREATMENTS AND EFFECTS ON COTTON

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### INTRODUCTION

Thermomechanical analysis (TMA) is a technique whereby the length of a substance, in an environment heated at a controlled rate, is recorded as a function of time or temperature. Much of the current interest in TMA is related to flame retardant finishes<sup>2</sup>. Thermal studies advanced rapidly after the end of World War II, adding to and improving methods used on non-textile materials. About the beginning of the sixties, thermal techniques used on inorganics and synthetic organics were adapted to textiles and films. Thermomechanical analysis of synthetic fibers was reported by Hall in 1962<sup>1</sup>. Study of fibers fused into loops and tested under constant stress was reported by Miller in 1968<sup>4</sup>. Thermal shrinkage of polyester was reported by Ribnick in 1969<sup>8</sup>. Total analysis of a polymer was discussed in a paper by Miller in 1972<sup>5</sup>. Thermomechanical analysis and other thermal methods were reported on flame retardant cottons by Weiss, Wade, and Andrews in 1974<sup>10</sup>. Thermomechanical analysis was used to study the non-isothermal stress relaxation of cotton/polyester blends treated with flame retardants and reported as part of a symposium in 1974<sup>7,9</sup>.

### EXPERIMENTAL

The thermomechanical analysis system used in this study was a commercial unit marketed by duPont. Figure 1 is a block diagram of the system used. The 990 console consisted of an x-y plotter and temperature programmer with related controls, the 942 TMA module equipped with a fiber probe to measure length changes in textile yarn, a 916 computer interface-digitizer converter, and a teletype equipped with a paper tape punch. The x-y graph was used to screen samples and set conditions while the actual runs of interest were recorded on paper tape and later computer processed.

The yarn sample was mounted between jaws by attaching two metal balls a half inch apart on the yarn. The sample was surrounded by a heater and then enclosed in a glass chamber. The atmospheres were nitrogen, oxygen, or carbon dioxide admitted from the top of the chamber to blanket the sample. Addition of weight was used to apply constant tension to the sample and was a standard two grams except as noted. Rate of heating was controlled to produce a linear temperature rise, and was 20 degrees per minute except as noted.

## RESULTS

Three basic patterns were observed using the visual graph obtained on temperature calibrated paper and are defined as type I which is simple elongation or contraction to failure, type II which is elongation to a critical temperature followed by contraction to failure, and type III which is a complex trace containing several regions of interest. Typical traces of each type are shown in Figure 2.

The controlled variables in the system, excluding sample and treatment selection, were applied load, rate of heating, and atmosphere. The effect of these variables on cotton are given in Table I.

Cotton generally produced a type II graph. The graph of type II had a uniquely observable point at the maximum elongation just prior to contraction to failure (ETC). The temperature of the ETC point in cotton occurred around 350°C. Thermogravimetric analysis of cotton shows 50% weight loss by 350°C. Differential thermal analysis of cotton shows no significant change until about 300°C when an endotherm of significance was observed using a nitrogen atmosphere or an exotherm observed with an oxygen atmosphere. Both the endotherm and the exotherm are due to decomposition of cotton cellulose. It is proposed that the elongation was attributable to hydrogen bond breakage and decrystallization of the cellulose polymer while the contraction was due to decomposition of the cellulose polymer.

The effect of increasing load on cotton was observed as an alteration of the thermal response from type II graph to type I graph. The contraction of the fiber under constant weight-load was a measure of the force due to decomposition. The force generated due to decomposition was greater than 450 and less than 1350 times the sample weight (Runs 1,2). The contraction can be prevented by applying a sufficient load, but this does not prevent decomposition. Unfortunately, the present state of the art does not allow one to follow both the chemical and physical changes simultaneously on the same sample.

The rate of heating did not alter the pattern of thermal response for pure cotton but the ETC point increased with heating rate similar to TGA and DTA observations.

The choice of atmosphere controlled the decomposition of the polymer. Nitrogen atmosphere allowed no real oxidative effects since the only oxygen available was that from the sample. Oxygen atmosphere was expected to promote autoignition<sup>3</sup>. Carbon dioxide atmosphere was selected as a comparison since it is one of the products of decomposition which could have an effect on the decomposition mechanism. The oxidative process under thermal conditions is a complex one as has been indicated in standard textbooks<sup>11</sup>. Autoignition of the gaseous combustibles generated by the cellulose decomposition occurred and was observed at a temperature as low as 330°C. The thermal response under both nitrogen and carbon dioxide are essentially the same. Studies to correlate thermomechanical changes with changes in composition of a 2 component atmosphere were desirable, and have been started, but are as yet incomplete.

Alteration of thermomechanical response can give valuable information on treatments used in textile processing. Earlier, the cotton pattern was changed from type II to type I by application of tension on the sample. This kind of data is useful in determining failure that can occur under distress conditions associated with fires. Insight can be gained in other more common treatments of cotton and textiles using thermomechanical and other related thermal methods. Consider the treatment of cotton with water. Cotton fibers stretched while wet with water and dried under stress exhibit an important response on rewetting known as swelling recovery<sup>6</sup>. This means that fabrics dried under deformation and processed into garments will deform to some extent when washed. The thermal response of a wet cotton yarn dried under 20 grams tension was observed as type I. This shows mutual fiber components are involved in water swelling-wetting process and in the load bearing process. It shows that increased organization of a fiber to bear load altered the response type. It further implies that thermomechanical analysis is measuring the resultant characteristics of the overall structural assembly and identification of structural differences may lead to a basic understanding of the two simple response types. The effect of drying was observed as a heating process. The response was essentially type II except for a contraction due to drying. This is another case of contractive force which can be estimated by applied load. The contractive force was greater than 2700 times the sample weight showing that it is greater than the contractive force observed in decomposition.

#### CONCLUSIONS

Thermomechanical analysis was shown to be effective as a tool to study textiles and textile treatments. Alteration of thermal response was shown by increasing the applied load-weight, physical treatment, and chemical treatment. Thermomechanical response was always observed during polymer decomposition.

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Table I. Cotton Yarns Under Loads, Heating Rates, and Atmospheres

Run #	Sample	Applied weight	Heating rate	Atmosphere	ETC 2/ deg	Elongation Failure	Type
1	12/3 cotton yarn	(gram) 2	deg/min 50	oxygen	(%) 341	(deg) 2.7	II
2	" " "	2	50	oxygen	---	345 334	I
3	12/2 (twist 4.25 dewaxed)	2	5	nitrogen	349	5.5	II
4	" " "	2	20	nitrogen	372	4.5	II
5	" " "	2	50	nitrogen	391	4.7	II
6	12/3 cotton yarn	2	20	nitrogen	360	5.9	II
7	" " "	2	20	oxygen	334	2.3	II
8	" " "	2	20	carbon dioxide	374	2.1	II
9	wet yarn dried under 20 g. wt.	2	20	oxygen	---	0.11/	I
10	water wet 12/3 cotton yarn	2	20	nitrogen	63 2/	0.9 2/	II
11	" " "	5	20	nitrogen	56 2/	0.9 2/	II
12	" " "	10	20	nitrogen	98 2/	0.4 2/	I
13	KSCN in liquid NH <sub>3</sub> /dried	2	20	oxygen	341	7.9	III

1/ Elongation at failure.

2/ Temperature and percent shrinkage (max) due to drying.

3/ Maximum elongation at this temperature.

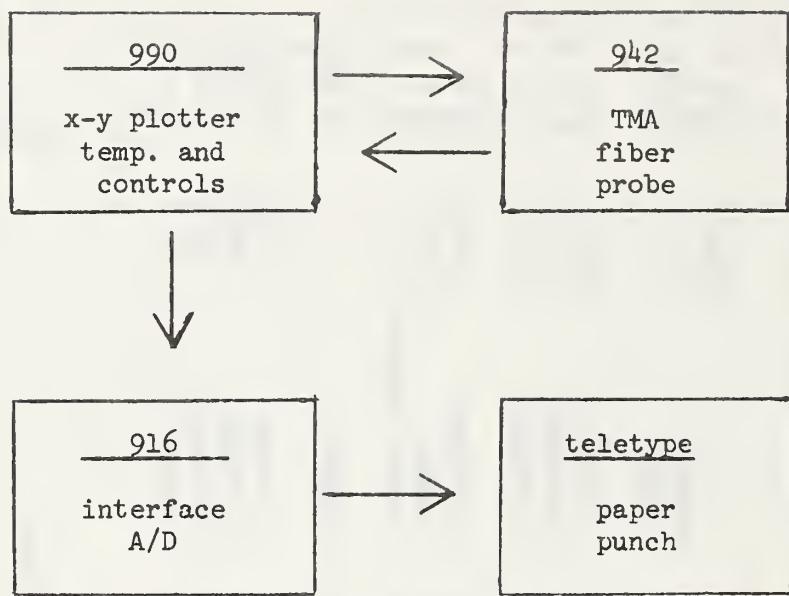


Figure 1--TMA system

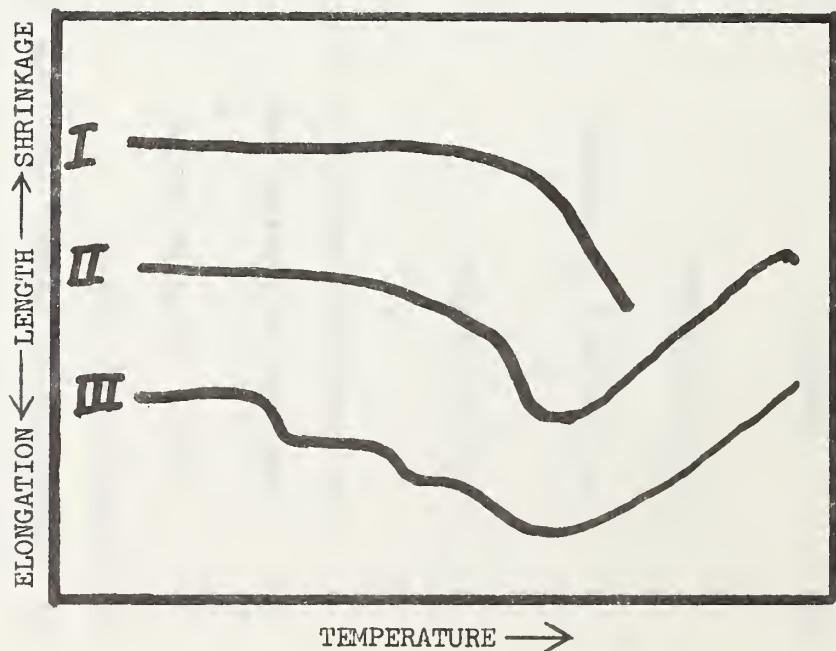


Figure 2--Typical curves

## LOCATION OF FINISHING MATERIALS IN FIBERS BY ENERGY-DISPERSIVE X-RAY ANALYSIS

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Southern Regional Research Center

## INTRODUCTION

An objective of microscopical analyses of chemically treated textile fibers has been to determine localities of interactions of chemical finishes and fibers. Scanning electron microscopy (SEM) readily shows deposits on fabric or fiber surfaces. Transmission electron microscopy techniques including changes in solubilities, heavy metal staining, and microincineration can indirectly indicate penetration into the fibers. Differential dyeing shows finish location by color variation in light microscopy (LM).

The new technique of energy dispersive x-ray (EDX) analysis provides a more direct method for location of such deposited or reacted elemental species. In combination with SEM, this technique permits mapping of elements in and deposited on fiber cross sections. EDX analysis utilizes the interactions that occur when matter is bombarded with an electron beam.

EDX Analysis Theory: An image is formed by the scanning electron microscope when a specimen is bombarded with an electron beam. Interaction of this beam with the subatomic structure of the specimen generates several types of radiation. Figure 1 illustrates the generation of backscattered and secondary electrons, photons, and x-rays. Information retrieved depends on the type of detector used. Secondary electrons emitted from the bombarded specimen are generally collected to form the SEM image, which may be readily identified since spatial detail is presented in a form similar to that seen with the naked eye.

Readjustment of electron energy levels after electron emission produces x-rays with energies characteristic of the particular elemental species. Collection of these x-rays and identification of their energies thus identifies the element from which they were emitted. When the x-ray information is fed through the cathode-ray display tube of the microscope, a distribution image is formed. Single elements are detected by adjusting the analyzer to the energy level of the element of interest. When an x-ray of this energy is detected a point is brightened on the display tube. The resulting image corresponds spatially to the specimen observed, with the density of dots related to elemental abundance.

Procedures: Of major importance in microscopical x-ray analysis of finished textiles is determination of the presence of the finish in the internal areas of the fiber. This may be accomplished by cutting thick (5 to 20  $\mu\text{m}$ ) yarn cross sections and analyzing cut surfaces.

In this study two different procedures were used to prepare fiber cross sections. Choice of procedure depends on equipment available and aim of the analysis. One procedure involves the Hardy sectioning technique often used in LM. This method is preferable for providing EDX analysis of fiber sections that have been studied previously by LM dyeing techniques. To produce Hardy sections, fibers were packed into a Hardy

hand microtome, sliced smooth at the surface, and coated with a nitro-cellulose lacquer. Sections cut with a razor blade are held together by the thin lacquer film. For LM this film is invisible in the mineral oil mounting medium and does not interfere with photography. However, in the scanning microscope the film is not only visible but reduces visibility of the sectioned yarn. Thus its removal is necessary. This procedure must be carried out with extreme care since the film stabilizes spatial positions of the fiber sections, and its removal might result in displacement of the sections to a point such that they cannot be related to LM photographs. In addition, if the fiber section bundle has been cut and mounted in mineral oil on a glass slide for LM, it is necessary to remove the mineral oil in preparation for SEM and EDX analysis. This was accomplished by lifting the cover glass and removing the lacquer-coated section bundle with forceps. The bundle was then washed in a warm phosphate-free detergent solution, rinsed in deionized water and placed lacquer-side down on a carbon disc used for EDX analysis. To remove the lacquer, ethyl alcohol was dropped on the edge of the carbon disc from a micropipette and allowed to flow gently across the surface. The disc was then placed in a petri dish containing alcohol and covered so that vapors completed the solvent extraction. The disc was observed under the wide field microscope periodically for 1/2 hour to determine progress of freeing the sections. If solvent action is allowed to become too drastic or is carried out for too long a time the sections will scatter.

The second procedure utilizes the methacrylate embedding technique used to cut ultrathin sections. A yarn was placed on a glass slide and coated with poly(butylmethacrylate) that was allowed to harden in an oven at 65° C. The embedding was thickened by addition of a 3/2 mixture of prepolymerized methyl and butyl methacrylates. After hardening, the embedded specimen was removed from the glass slide and trimmed for sectioning in a flat vice on a Porter-Blum MT-1 microtome. Thick sections were cut with a diamond knife by setting the thickness dial on the microtome to a maximum and, using the bypass arm, rotating the embedding through 6 to 8 turns before allowing it to pass over the knife. Variation in microtomes makes this setting arbitrary; thus, experimentation with thickness settings for desired section thickness is necessary when various microtomes are used. After collection in the boat, sections were picked up with an eye lash mounted on a toothpick, and placed on a carbon disc. The methacrylate embedding medium was removed by placing the discs in a petri dish on filter paper saturated with methyl ethyl ketone. The disc was closed, placed in a desiccator and allowed to remain approximately 24 hours. Since it is normally advantageous to provide an SEM image of the specimen in order to correlate x-ray data with fiber structure, the specimen was prepared for secondary image production. For this purpose textile materials must be coated with an ultrathin layer of a conductive material to prevent buildup of static charge on the specimen surface. This may be accomplished by evaporation of gold or gold-palladium to form a continuous surface film. However, presence of these metals interferes with x-ray analysis, consequently development of an alternate procedure was necessary. Carbon has been used as an aid in charge suppression and since it does not interfere spectoscopically, the carbon discs containing the embedding medium free sections were attached to specimen stubs with silver paste,

placed in a vacuum bell jar and coated with carbon. For these experiments a Cambridge Mk IIa scanning electron microscope with an EDAX x-ray system was used.

The carbon discs were scanned in the microscope to find groups of sections of interest and these were photographed prior to x-ray examination. Low accelerating voltage is normally used in SEM of textiles to prevent specimen damage and reduce the possibility of charging. Higher KVs may be required for x-ray analysis and resultant beam damage may make the specimen unsuitable for secondary image photography after x-ray mapping.

## RESULTS

Samples analyzed included all-cotton print cloth treated either with tetrakis(hydroxymethyl)phosphonium hydroxide (THPOH)-NH<sub>3</sub> or with THPOH-amide, and a cotton/polyester blended fabric treated with tetrakis(hydroxymethyl)phosphonium chloride (Thpc)-urea-poly(vinyl bromide) (PVBr). The THPOH-NH<sub>3</sub> finished fabric was treated in a bath of 40% solids and had a phosphorus content of 4.2%. Figure 2a shows an SEM cross section cut on an ultramicrotome, of fibers from this fabric. No flame-retardant chemical can be detected on this section except that adhering to the outer surface of the fiber. Figure 2b is the phosphorus x-ray map showing phosphorus distribution throughout the fiber section.

The second all-cotton sample was treated with THPOH-amide to a 15.3% add-on. Yarns from this fabric were dyed in a 1% aqueous solution of Acid Blue I (Erioglaucine Supra Conc.) for light-microscopy testing. Yarn sections were cut on a Hardy hand microtome. In LM the flame-retardant polymer is blue while the untreated fiber remains colorless. Differences in dye uptake were seen in the warp and fill directions and indicated that fibers in the outer portion of the yarn were thoroughly penetrated whereas those in the center were not. EDX analysis also showed phosphorus concentrated in the outer fibers but not in those in the center of the yarn. In contrast, yarns from the filling direction in this same fabric showed a light, but more uniform, penetration throughout the yarn.

The cotton-polyester fabric was treated in a Thpc-urea-PVBr bath containing 6.4% PVBr. The warp yarn was all cotton and the filling yarn was blended of cotton and polyester. EDX analysis showed the warp yarn to be thoroughly penetrated with the Thpc finish, with phosphorus distributed throughout the cotton fiber sections. The cotton sections from the blended filling yarn were also well penetrated with phosphorus (Fig. 3a), but no detectable phosphorus was found in the polyester. Bromine distribution maps (Fig. 3b) show concentrations of bromine in the polymer deposited on the outer surface of both cotton and polyester fibers, but any bromine within the fibers was not of high enough concentration to be detected.

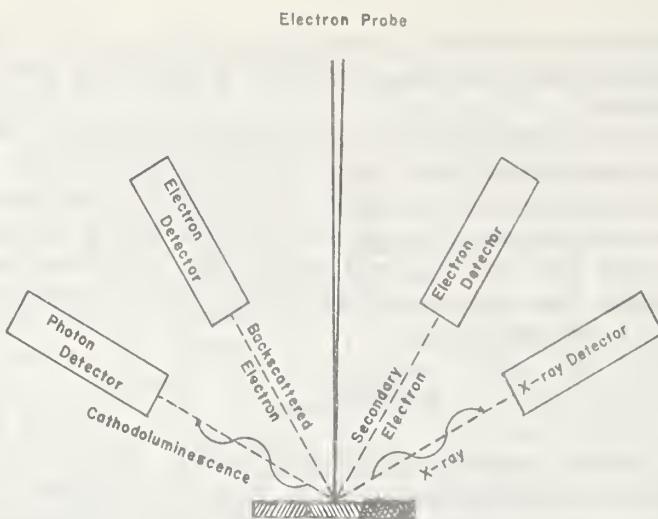


Figure 1. Information generated by electron probe



Figure 2a. Cross sections of cotton fibers treated with THPOH-NH<sub>3</sub> (SEM)



Figure 2b. X-ray map showing phosphorus distribution in cotton sections shown in 2a. White dots indicate phosphorus concentration



Figure 3a. Overlay of phosphorus x-ray map on scanning micrograph of cross sections of cotton and polyester fibers treated with Thpc-urea-PVBr



Figure 3b. Overlay of bromine x-ray map on scanning micrograph of cross sections of cotton and polyester fibers treated with Thpc-urea-PVBr

## RAPID ANALYSIS OF TEXTILE MATERIALS FOR TRACE METALS

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## INTRODUCTION

The determination of the inorganic impurities contained in cellulose can be very important since even trace amounts of some elements undesirably affect the properties of cellulose. For example, iron catalytically accelerates the oxidation of cellulose in alkaline solutions, and also may affect the dyeability, strength, photostability, thermostability and other properties of cellulose. Similar instances can be given for other elements. As a rule, the concentration of these elements foreign to cellulose is very low and as a result the determination of these elements can present considerable difficulties. Large amounts of cellulose must be carefully ashed, a tedious and time-consuming project, before conventional analyses may be performed.

Flameless atomic absorption offers an alternative method of determining metals present in low concentration. It has the advantages of being both rapid and extremely sensitive. In this report, the direct analysis of solid samples using the graphite furnace for flameless atomic absorption will be described. Little or no sample preparation is necessary. The concentration of element determined by direct analysis of the solid is compared with nitric acid extracts of the cellulosics and with flame atomic absorption analysis of the ashed cellulosics and x-ray fluorescence data where such data are available.

## EXPERIMENTAL

The equipment used in this study consisted of a Perkin-Elmer Model 306 double-beam atomic absorption spectrophotometer equipped with the HGA-2000 graphite furnace, a Model 56 recorder and a deuterium background corrector. Samples were weighed on a Cahn Model G electrobalance. Two techniques were used for the analysis - the direct analysis of the solid and the analysis of the nitric acid extract of the cellulosic. The pulps used were ground in the Wiley Mill prior to analysis. The cotton samples were cut with a scissors.

For the determination of metals directly on the solids, 0.5 mg or less was weighed into a tared tantalum boat and positioned in the graphite furnace by using the Perkin-Elmer solid sampling device. The sample was then dried, charred, atomized and the peak height recorded on a strip chart recorder.

In the extraction method, weighed amounts (approximately 2g) of the cellulosic were extracted overnight with 1 N HNO<sub>3</sub>. The extracts were filtered, the residue rinsed with deionized water and the filtrate and

washings were quantitatively transferred to 100 ml volumetric flasks and brought to volume with deionized water. Aliquots of the extracts were introduced into the graphite furnace by using Eppendorf microliter pipettes and were analyzed under the same conditions used for the solids.

Experimental conditions for the determination of copper were: drying, 30 sec at 100° C; charring, 60 sec at 900° C; and atomizing 10 sec at 2500° C. The sensitivity at the 325 nm wavelength was 50 pg/0.0044 absorbance. The sensitivity at the 249.9 nm wavelength was 4000 pg/0.0044 absorbance.

Operating parameters for manganese were similar to those for copper: drying, 30 sec at 100° C; charring, 60 sec at 1000° C; atomizing, 10 sec at 2400° C. Two wavelengths were also used to determine manganese. Sensitivity was 8 pg/0.0044 absorbance at 279.5 nm and 87 pg/0.0044 abs at 403 nm.

The operating parameters for iron were: drying, 30 sec at 100° C; charring, 75 sec at 1100° C; atomizing, 10 sec at 2500° C. The wavelength used was 302 nm and sensitivity was 115 pg/0.0044 abs.

The conditions for cobalt were: drying 20 sec at 110° C; charring, 45 sec at 1000° C; atomizing, 8 sec at 2600° C. The wavelength used was 304 nm and sensitivity at this wavelength was 740 pg/0.0044 abs.

Standard aqueous solutions of appropriate concentrations were prepared fresh daily by dilution of stock 1000 ppm standard solutions obtained commercially.

The flame atomic absorption data were provided by ASTM Committee D23 from the round robin interlaboratory testing. The values given represent the mean from eight laboratories, but the interlaboratory precision was poor.

Results obtained by using the method of additions were essentially the same as those obtained using a standard curve prepared from aqueous standards. All values reported were based on the curve prepared from aqueous standards.

## RESULTS

The data obtained for the determination of manganese in six pulp samples are given in Table I. The concentration of manganese from the direct analysis of the solid is compared with nitric acid extracts of the pulps and with values obtained by flame atomic absorption analysis of the ashed pulp. Precision of the results for direct analysis of the solids is given. The concentration of manganese in the nitric acid extracts of the pulps showed good precision (the relative standard deviation was less than 10%) and agreed well with the flame atomic absorption results. For two samples, D23-1 and D23-2, the concentration of manganese was quite high and use of the less sensitive wavelength (403 nm) permitted the use of larger samples and thus reduced sampling and weighing errors.

Manganese was also determined on a series of cotton, polyester and cotton-polyester blends (Table II). The standard deviation and relative standard deviation are shown for the solid determinations. These are based on six replicate determinations for each sample. The nitric acid extracts were performed in duplicate for each sample and each duplicate is the average of at least three replicate determinations. The replicate determinations had a relative standard deviation of 8% and the duplicate determinations agreed well with each other and with the average from the solid determinations.

The data obtained for the determination of copper in the six pulp samples are given in Table III. The concentration of copper from the direct analysis of the solid is compared with the nitric acid extracts of the pulps and with values obtained by flame atomic absorption analysis of the ashed pulp. The concentration of copper in the nitric acid extracts of the pulps also showed good precision (again less than 10% relative standard deviation) and agreed well with the flame atomic absorption analysis of the ashed pulps. These values were somewhat lower than the values from direct analysis of the solid pulp, possibly as a result of copper contamination of the solid sample during grinding in the Wiley mill.

Some fabrics dyed with a copper dye, Procion Rubine HB-S, were analyzed using the direct solids determination (Table IV). In this case the concentration of copper was so high that a less sensitive wavelength 249.7 nm was used. The level of copper was high enough for x-ray fluorescence to be useful and the agreement between the flameless atomic absorption technique and x-ray values was very good.

Some fabrics dyed with a cobalt dye, Algal Brilliant Blue-4GP, were also analyzed using the flameless technique. (Table V). Samples dyed with three levels of dye were analyzed. The light colored fabric was uniformly dyed; however, the two darker fabrics had light and dark areas. Surprisingly, atomic absorption analysis of the light and dark areas showed no apparent difference in the level of cobalt. It may be that the eye is a much more sensitive indication of the dye than the instrument is of the cobalt or that the splotches were a surface effect so that when the complete thickness of fabric was analyzed the average values for the light and dark areas were the same.

The results obtained for iron are shown in Table VI. Overall, the agreement between replicate determinations was not as good for iron as for the other elements. Iron is a more common laboratory contaminant than manganese or copper and would be easy to introduce inadvertently during the determination. The pulp samples were not ground in the Wiley mill for this determination because of the danger of contamination with iron from the mill. Instead, a stiff tungsten wire was used to scrape fibers from the surface of the pulps.

In summary, flameless atomic absorption with the graphite furnace offers a rapid and very sensitive method for the determination of metals present in cellulosic materials. It is not without its difficulties, however. A major problem in obtaining reproducible results is lack of homogeneity of the sample. A number of replicate determinations (at least six) must be made to ensure obtaining an accurate answer. However, the graphite furnace can also be used to determine how uniformly a given element may be distributed throughout the cellulosic matrix. For many elements, the extraction procedure with 1N nitric acid is preferable since it eliminates the problem with distribution. The sensitivity of the flameless atomic absorption technique is such that even trace quantities of elements in the ppb range may be readily determined.

TABLE I  
Manganese Determination on Pulp Samples

Sample	ppm Mn (Solids)	No. Detns.	S(ppm)	CV (%)	ppm Mn (Extracts)	ppm Mn (Flame)
D23-1*	17.3	5	0.04	0.3	20.4	18.9
D23-2*	34.5	5	3.4	9.6	50.3	40.4
D23-3	2.3	6	0.3	13.0	2.2	2.0
D23-4	0.4	4	0.1	13.4	0.2	0.2
D23-5	2.3	7	0.5	20.4	2.1	1.5
D23-6	2.2	4	0.5	22.6	2.6	2.0

\* Determinations made at 403 nm; all others at 279.5 nm

TABLE II  
Mn Determination on Cotton, Polyester and Cotton/Polyester Blend

Sample	Solid Determination*			HNO <sub>3</sub> Extracts	
	C(ppm)	S(ppm)	rsd (%)*	ppm	Deviation(%)**
100% Cotton Fiber	3.0	0.2	5	3.3	9
100% Polyester Fiber	0.4	0.1	25	0.04	25
50/50 Cotton/PE Sliver	1.6	0.3	17	1.2	5
100% Cotton Knit--Greige	2.3	0.4	16	2.3	2
100% Polyester Knit--Greige	0.2	0.07	40	0.1	-
50/50 Cotton/PE Knit--Greige	1.3	0.3	24	1.0	9
100% Cotton Knit--Bleached	0.8	0.2	30	0.4	15
100% Polyester Knit--Bleached	0.3	0.06	22	0.1	8
50/50 Cotton/PE Knit "	0.9	0.5	50	0.3	15

\* Six replicate determinations

\*\* Duplicate determinations

TABLE III  
Copper Determination on Pulp Samples

Sample	ppm Cu (Solids)	No. Detns.	S(ppm)	CV (%)	ppm Cu (Extracts)	ppm Cu (Flame)
D23-1	1.8	10	0.4	20.8	0.8	<1.0
D23-2	1.0	5	0.3	27.4	0.5	0.8
D23-3	1.8	6	0.1	7.8	0.6	0.5
D23-4	1.8	5	0.2	11.7	0.5	0.5
D23-5	1.4	8	0.3	22.8	0.6	0.7
D23-6	1.2	5	0.2	12.2	0.1	0.5

TABLE IV

Determination of Copper on Fabrics Treated with Procion Rubine HB-S Dye

<u>Sample</u>	<u>% Cu (AA)</u>	<u>% Cu (X-Ray)</u>	<u>Add-On (%)</u>
I	0.03	0.03	0.4
III	0.09	0.12	0.8
III	0.13	0.13	1.7

TABLE V

Determination of Cobalt on Fabrics Dyed with Algal Brilliant Blue 4-GP

<u>Sample</u>	<u>% Co (AA)</u>	<u>% Co (X-Ray)</u>	<u>Add-On (%)</u>
I	0.04	0.02	0
II-Light	0.14		
II-Dark	0.15	0.08	0.5
III-Light	0.18	0.12	0.9
III-Dark	0.17		

TABLE VI

Iron Determination on Pulp Samples

<u>Sample</u>	<u>ppm Fe (Solids)</u>	<u>S (ppm)</u>	<u>CV (%)</u>	<u>ppm Fe (Extracts)</u>	<u>ppm Fe (Flame)</u>
D23-1	6.3	0.7	11.3	8.1	10.8
D23-2	9.3	3.0	32.8	5.9	12.7
D23-3	9.0	5.7	63.6	12.6	6.6
D23-4	2.1	0.5	22.2	8.3	4.7
D23-5	9.8	5.6	56.7	6.3	6.5
D23-6	7.4	2.3	30.1	5.1	3.5

## THE PLASTICITY OF THE COTTON HAIR

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## INTRODUCTION

The cotton hair is inelastic in that a perceptible longitudinal strain produced by a conventional longitudinal stress is not completely recovered when the stress is removed. This is illustrated by data shown in Table I. In some instances, when the stress was applied continuously for several days, the hair was eventually pulled apart. The cellulose in the hair has the appearance of flowing under stress, and some may interpret this behavior as an irreversible lengthwise slippage of fiber over fiber.

It was concluded that the elastic limits of the hair are not exceeded when a very small strain is induced by simply twisting the hair through a small angle about its axis. We observed no permanent deformation under such conditions--the angle of strain returned to zero when the torque was removed. It should be possible, therefore, to estimate the elasticity constants of the cellulose in the cotton hair when one end is attached to a solid support and a weight is attached to the distal end, and the system is induced to behave as a torsion pendulum.

We set up such an arrangement, with a mirror attached to the weight so we could determine both the period of oscillation and the amplitude (Figure 1). Motion was induced without causing the weight to swing in a pendulum fashion. A strongly damped oscillatory motion was observed. The application of the second law of motion to this system is expressed as:

$$\frac{d^2\phi}{dt^2} M + 2b \frac{d\phi}{dt} + k^2\phi = 0 \quad (1)$$

when d'Alembert's principle is applied. Here  $\phi$  is the angle of twist,  $M$  is the moment of inertia,  $t$  is the time,  $k^2$  is a force of restitution that is proportional to the angle of twist, and  $b$  is a damping constant. The fact that the harmonic motion is damped means that the second term in equation (1) is the expression of a resistance force that is proportional to the rate of twist, and therefore the constant  $b$  has the properties of a viscosity. This is distinguished from a frictional resistance which is not dependent on the rate, e.g., the sliding of iron over iron.

We divide equation (1) by  $M$ . The resultant auxiliary equation will have the roots

$$-\frac{b}{M} \pm \sqrt{\left(\frac{b}{M}\right)^2 - \frac{k^2}{M}}$$

and hence the general solution of equation (1) is

$$\phi = \phi_1 e^{t \left( \frac{-b}{M} + \sqrt{\left( \frac{b}{M} \right)^2 - \frac{k^2}{M}} \right)} + \phi_2 e^{t \left( \frac{-b}{M} - \sqrt{\left( \frac{b}{M} \right)^2 - \frac{k^2}{M}} \right)} \quad (2)$$

The boundary conditions are set up in our experiments so that  $\phi = \phi_0$  when  $(d\phi/dt) = 0$  and  $t = 0$ . Moreover,  $k^2/M$  must be larger than  $(b/M)^2$ , for otherwise there would be no oscillatory motion, and therefore the expression

$$\sqrt{\left( \frac{b}{M} \right)^2 - \frac{k^2}{M}}$$

is imaginary. Under these circumstances, and subject to the boundary conditions, the specific solution of equation (1) that applied is

$$\phi = \phi_0 \sqrt{\frac{k}{\left( \frac{k^2}{M} - \frac{b^2}{M} \right)^2}} e^{-\frac{bt}{M}} \sin t \sqrt{\frac{k^2}{M} - \left( \frac{b}{M} \right)^2} \quad (3)$$

This equation describes a damped sinusoidal motion with a period of

$$T = \frac{2\pi}{\sqrt{\frac{k^2}{M} - \left( \frac{b}{M} \right)^2}}$$

and an amplitude that decreases exponentially as

$$e^{-\frac{bt}{M}}$$

and we are supplied with a means of determining both b and k. Thus, b provides a measure of the dissipation of energy that occurs when a mass of cellulose undergoes a deformation, such as bending or twisting. The constant k contains both the shear modulus and Young's modulus, and the calculations of these constants will be reported at another time. Attention in this report is limited to the constant b.

In all of our experiments we used the same weight at the distal end of the hair--this had a moment of inertia of  $0.0606 \text{ g cm}^2$ . Of course, the lengths of the several hairs used were not all the same, but it was established in tests with nichrome wire that the square of the period of oscillation is proportional to the length of the suspending wire, and thus it is possible to convert the period observed with a given hair to that

of a hair of standard length. We chose 2 cm as the standard length. We calculated  $b$  through use of the regression of the log of the angle (in radians) of the maximum amplitude on time where the units of time were integral multiples of the period. Coefficients of correlation between  $\log \theta$  and  $T$  were found to range from -0.992 to -0.999 for 6 and 7, and sometimes 8, degrees of freedom, so the agreement between theory and observation is good.

The experimentally determined value of  $b$  is influenced by the cross section of the hair. A weakness in the present report is the absence of these data, and we ascribe variations in the values of  $b$  to variations in this area. Our intuitive conclusion is that  $b$  [ca.  $1.8-7.6 \times 10^{-4}$  g/s] is an intensive property of cellulose.

The influence of the relative humidity in the chamber where the hair is suspended is of interest, as is the influence of mercerization. Typical data for cotton hair from two different lots of cotton are shown in Table II. The analysis of variance of these data reveals that neither the relative humidity nor mercerization influences the value of  $b$ .

The difference due to the lot of cotton hair is probably due to the difference in the degree of fineness of the hair.

Table I

Behavior of a cotton fiber under stress.  
 Area of cross section of fiber estimated as being  $127 \times 10^{-8} \text{ cm}^2$ .  
 Original length of fiber (stress of 0.284 g) 2.158 cm.

Time (min.)	wt added to 0.284 g.	length of fiber (cm.)	change in length (cm.)	Young's modulus calculated (in-lb-sec system)
0	0 g	2.158	0.000	----
1	0.2	2.158	0.000	----
360	---	2.174	0.016	$9.75 \times 10^6$
361	-0.2	2.174	0.000	----
367	1.0	2.194	0.020	2.79
372	-1.0	2.190	-0.004	----
1087	---	2.190	---	----
1088	1.0	2.194	0.004	2.79
2167	---	2.240	0.046	1.34
2887	---	2.320	0.080	0.71
4327	---	2.320	---	----

Table II

Influence of relative humidity and mercerization on the damping constant of cotton fibers.\*

Lot # 132			Lot # 931	
Relative humidity %	Native	Mercerized	Native	Mercerized
42	1.8	2.3	3.2	4.4
50	2.4	2.4	2.6	4.0
65	5.4	2.6	3.2	7.6
80	4.2	2.3	6.4	3.4
95	2.6	2.3	4.4	5.7
Source of variance				
	Mean square		Degrees of freedom	F ratio
Relative humidity	1.52	4	not significant	
Mercerization within lots	1.50	2	"	
Between lots	13.78	1	8.5 [Sig. at 0.025 level]	
Residual	1.62	12		

\* The power of 10 for the value of  $b$  is excluded for simplicity in comparison.

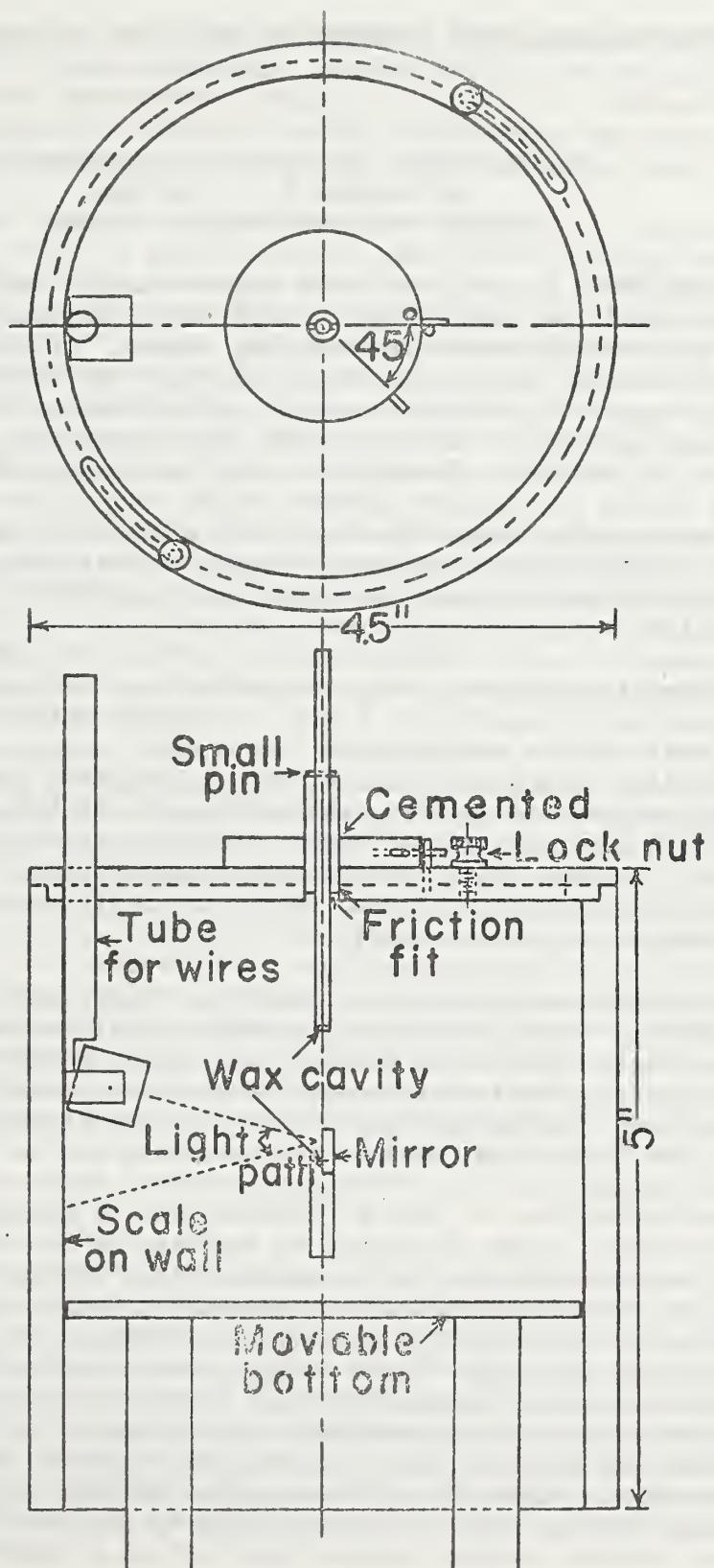


Figure 1--Apparatus used in measuring the amplitude and period of oscillation with the cotton hair serving as a part of a torsion pendulum.

## FACTORS AFFECTING CATALYTIC ACTIVITY IN CELLULOSE CROSSLINKING REACTIONS

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For many years it has been known empirically in the textile industry that certain salts are better than others for catalyzing the reaction of cellulose with methylolamide crosslinking agents. Although a remarkable number of salts are possible as catalysts, very few have achieved much commercial usage. For several reasons, mostly related to health, environmental protection and pollution, it now appears that the usage of even that few is in jeopardy. In addition, fuel and energy shortages have prompted a search for catalyst systems which will allow reactions to take place at lower curing temperatures and shorter curing times, and alternative, energy-conserving systems are being sought. It has been reported (1) that reducing the conventional curing temperature about 20°C can afford a fuel savings of 10%.

A systematic study of pad-dry-cure finishing of cotton fabrics with several crosslinking agents and a wide variety of salts was undertaken to determine what factors contribute to and control catalytic activity (2). In the generally accepted mechanism, the crosslinking reaction is believed to proceed through catalysis by either hydrogen ion (Brønsted acid) or a metal ion with a vacant orbital capable of accepting a pair of electrons (Lewis acid). It was found in this study that either or both of these mechanisms can be operative at the same time to different extents depending upon the particular salt employed.

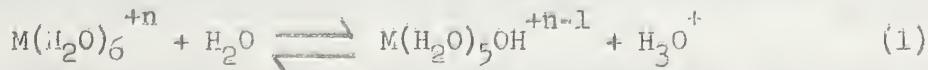
Crosslinking agents used were dimethyloldihydroxyethyleneurea (DMDHEU), dimethylolethyleneurea (DMEU), or dimethylol ethyl carbamate (DMEC). After finishing, treated fabrics were washed and analyzed for bound nitrogen and wrinkle recovery. Plots were made of catalyst concentration in the pad bath vs. nitrogen and wrinkle recovery (expressed on a % yield basis, i.e., percent of the theoretical maximum nitrogen that can be introduced or percent of the maximum wrinkle recovery improvement that can be attained). Three distinct features of such plots were used to assess catalytic activity: the initial slope, which is related to the rate of the reaction; the level off point, which is related to the maximum yield obtainable from the reaction; and the minimum concentration necessary to achieve maximum reaction (cf. Figure 1). No one factor is completely adequate for comparing activities among catalysts. Although Figure 1 shows bound nitrogen as a function of catalyst concentration, similarly shaped curves are obtained when catalyst concentration is plotted against other properties of the finished fabric, both chemical and physical, which are directly related to the extent of reaction which has taken place, for example, wrinkle recovery angle or durable press rating. This is demonstrated by the data shown in Figure 2. In general, wrinkle recovery curves level off at a lower value than nitrogen

curves simply because it is easier to approach 100% reaction between cellulose and the nitrogen-containing compound than it is to achieve 100% wrinkle recovery improvement (total of 360° W + F). However, the general trends in catalytic activity among salts remain the same, and similar comparisons can be made regardless of the parameter used.

The first area studied was the effect on catalysis of varying the cation in the salt within a given periodic group while holding the anion constant. Data from treatments with the group II A chlorides are shown in Figure 3. All three factors used to assess catalytic activity--slope, level-off point, and minimum concentration--indicate that catalytic activity decreases as the atomic number increases within a given group. These results could be due to several factors, among them are increasing basicity of the metal ion and increasing ionic size which would limit the mobility of the metal ion to the reaction sites.

Klein and Bingham (3) have shown that at conventional curing temperatures,  $MgCl_2$  does not thermally break down to yield HCl (a Brønsted acid). Furthermore, Cotton and Wilkinson (4) report that primarily ionic salts, such as  $MgCl_2$ , do not undergo appreciable hydrolysis in aqueous solution to yield HCl and a metal-hydroxy complex. Thus it appears that salts of group II A metals must catalyze crosslinking reactions primarily by way of a Lewis acid mechanism.

Results obtained with the II A metal chlorides can be both compared and contrasted with results from chlorides of the more covalent group II B metals; zinc, cadmium, and mercury. The overall catalytic activity of the II B salts was higher than their corresponding II A salt (i.e.  $Zn > Ca, Cd > Sr$ , and  $Hg > Ba$ ). As with group II A salts, a general decrease in catalytic activity was observed as the atomic number increased within the group. However, the magnitude of the decrease was not as large as that noted with the II A salts. The fact that decreases do occur can be explained by factors similar to those given above. However, the smaller magnitude of the decreases is a result of the more covalent nature of group II B salts. It has been demonstrated (4) that ions from covalent salts undergo hydrolysis reactions in aqueous solution as follows:



These reactions give rise to hydrated metal-hydroxy complexes and yield hydronium ions which can add Brønsted acid catalysis to an already existing Lewis acid mechanism, thereby increasing overall catalytic activity. The greater the covalent character of the salt, the greater the tendency to undergo hydrolysis. Because of its small size and molecular weight and very rapid mobility compared with the heavier metal ions, the hydrogen ion liberated provides such strong catalysis that its presence exerts a leveling effect so that differences in catalytic activity among members of the group II B are small; considerably less pronounced than among the group II A counterparts.

An ionization constant for equation 1 can be written:

$$K_a = \frac{[M(H_2O)_5OH^{+n-1}][H_3O^+]}{[M(H_2O)_6][H_2O]} \quad (2)$$

Equation 1 depicts the first ionization only, although subsequent ionizations are indeed possible, as well as other reactions to form polynuclear bridged species, each of which is capable of liberating more hydrogen ion.

To test the hypothesis of Brønsted catalysis being operative in addition to Lewis acid catalysis, experiments were run using the chloride salts of Al, Cr, and Fe. All three metal ions had the same oxidation state, +3, and the same anion. Concentrations, time and temperature of cure were all constant. The only difference is the abilities of the three metal ions to undergo hydrolysis ( $K_a$ 's are: Al  $1.12 \times 10^{-5}$ , Cr  $1.26 \times 10^{-4}$ , and Fe  $6.30 \times 10^{-3}$ ). Results showed that the order of catalytic activity directly correlated with the ionization constants (i.e. Fe > Cr > Al). In addition, the magnitude of the catalytic activity was of significance. All three salts exhibited much greater activity than any of the group II A or group II B salts. For example,  $AlCl_3$  promoted a 20% reaction yield at a catalyst concentration of 0.01 mmol./100 g of pad bath, a weight percent of only 0.002%.

The high degree of catalytic activity exhibited by the +3 salts prompted a study of the effects of oxidation state of the cation on catalytic activity. A set of cotton printcloth samples was treated with DMDHEU and the nitrate salts of  $Ag^{+1}$ ,  $Cd^{+2}$ , and  $In^{+3}$ , while another set was treated with DMDHEU and the chloride salts of  $Cd^{+2}$ ,  $Al^{+3}$ ,  $Sn^{+4}$ , and  $Sb^{+5}$ . In all cases, as the oxidation state of the metal ion increased, the catalytic activity of the salt increased, other parameters being held constant. Salts with oxidation states above +3 were extremely active, almost to the point of indistinguishability between the +4 and +5 salts. This effect too can be explained on the basis of hydrolysis of the hydrated metal ions which gives rise to Brønsted catalysis as well as Lewis acid catalysis. As the oxidation state increases, the covalent character of the salt also increases, distributing the charge from the central metal ion out onto the ligand water molecules thereby increasing their potential toward ionization.

The effect of the anion of the salt on the activity of the catalyst was also investigated. Figure 4 shows results from experiments in which cotton printcloth samples were given pad-dry-cure treatments with DMDHEU and various magnesium salts as catalysts. With the halides, a small, general decrease in activity was observed in going from chloride to bromide to iodide. Similar experiments with zinc halides showed them to be essentially equivalent with regard to rate, level-off nitrogen, and maximum concentration to achieve maximum reaction. This equivalence is presumably due to the leveling effect that hydrolysis and subsequent Brønsted catalysis have on the reaction.

Among the magnesium salts studied, the fluoborate showed the fastest rate, whereas the nitrate had a slightly higher yield. Magnesium sulfate exhibited an exceptionally poor rate and reaction yield and consequently would be an unacceptable DP catalyst. Similar results and conclusions were obtained from experiments with the corresponding zinc salts, except that zinc sulfate did not have the drastically reduced activity exhibited by magnesium sulfate. This difference is attributed to Brønsted acid catalysis caused by hydrolysis reactions of the zinc salt. Based on the results obtained with the group II A halides, it would be expected that the activities of the sulfates of the other members of group II A metal ions would be even lower than that of magnesium. However, this hypothesis could not be tested experimentally due to the insolubility of the other group II A sulfates. Based on work with magnesium, zinc, and cadmium salts, anions can be ranked according to activity as follows:



In general, activities of the salts of a given metal ion follow the acid strengths of the free acids corresponding to the anions.

Results obtained in experiments with various cations indicate that some salts function as catalysts primarily by way of a Lewis acid mechanism, while others operate with both Lewis acid and hydrogen ion catalysis. Changes in temperature affect both the kinetic energy and ionic mobility of ions. Therefore, small changes in curing temperature should have a much greater effect on those catalysts which operate by Lewis acid mechanism than those which also catalyze by hydrogen ion since the mobility of the hydrogen ion is approximately six times greater than that of most of the metal ions studied. To test this hypothesis fabric samples were given pad-dry-cure treatments with DMDHEU and either calcium nitrate (group II A - Lewis acid) or zinc nitrate (group II B - Lewis and Brønsted) as catalyst. Curing was carried out at four different temperatures: 160, 150, 140, and 130°C. The results are shown in Figure 5. At all temperatures, the catalytic activity of the group II B salt was higher than the corresponding group II A salt, because both mechanisms were operative. As the curing temperature was lowered from 160° to 130°, the catalytic activity of zinc nitrate was only slightly reduced in terms of reaction rate. With calcium nitrate, activity was drastically reduced both in terms of rate and reaction yield. These results are in agreement with the differences in mechanisms postulated for the two classes of catalysts.

Another question under investigation during the course of this work was: "Is the catalytic activity of a given salt dependent upon or independent of the concentration of crosslinking agent in the padding solution?" To elucidate this point, fabric samples were treated with aqueous solutions containing 4.5, 9, 13.5, and 18% DMDHEU each with various concentrations of either zinc nitrate or magnesium chloride as catalyst (cf. Figure 6). The data for magnesium chloride show that for maximum reaction (yield) to be attained, a certain minimum molar ratio of magnesium chloride to DMDHEU must be maintained, and that ratio (approximately 0.07) is the same

regardless of the concentration of crosslinking agent in the treating bath. Also, as seen in Figure 6, the maximum yield attained is decreased as the crosslinking agent concentration is increased. That is, it is easier to approach 100% reaction in treatments with dilute solutions than with more concentrated. Similar results were obtained with zinc nitrate.

With either Lewis acid catalysis or Brønsted acid catalysis, the proposed mechanism operates through formation of a resonance stabilized carbonium ion which undergoes nucleophilic attack by a cellulosic hydroxyl, followed by loss of a proton to form the cellulose ether. The proton released has two possible paths to follow. It can either protonate the metal-hydroxy complex formed in an earlier step, split off a molecule of water and regenerate the metal ion with a vacant orbital (Lewis acid mechanism); or, it can directly protonate another available methylol oxygen (Brønsted acid mechanism). The path taken will depend upon the relative basicities (electron density) of the metal-hydroxy oxygen and the methylol oxygen. Electron density of the metal-hydroxy oxygen will be influenced by the nature of the metal ion. Electron density on the methylol oxygen is affected by inductive effects of the particular substituent groups in the crosslinking agent. All of the experimental results reported thus far, and all of the conclusions drawn and general trends established have been based on work with one crosslinking agent, DMDHEU. To test the validity of these conclusions, similar experiments were conducted with two other crosslinking agents, DMEU and DMEC, with various salts as catalysts. In all cases, the same general catalytic trends noted among the various salts were observed regardless of the agent employed, i.e. group II B salts more active than their group II A counterparts; decreases in activity with increasing atomic number within a given group, etc. The only differences noted were in the absolute values of the reaction rates, reaction yields, and concentration minima. These varied with the particular agent used, with DMEU generally showing the highest reactivity and yield, followed by DMDHEU, followed by DMEC. A typical example of the results is shown in Figure 7. Ranking of the various salts according to catalytic activity was unaffected by the nature of the methylolamide.

In summary, it was found that catalytic activity is a complex result of several contributing factors including: acidity and oxidation state of the cation, nature of the anion, ionic size and ionic mobility, and hydrolysis reactions which the salts may undergo in aqueous solution. Both Lewis acid and Brønsted acid (hydrogen ion) mechanisms are concurrently operative to different extents with different catalysts.

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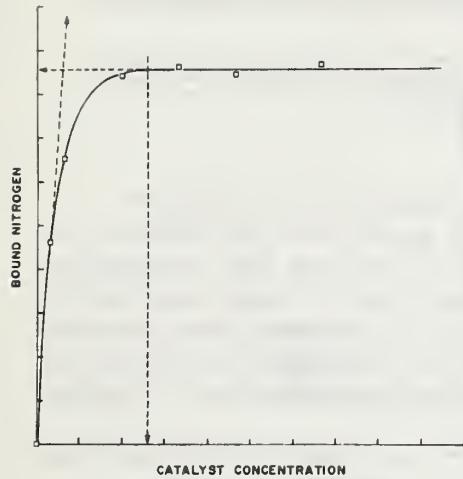


Figure 1

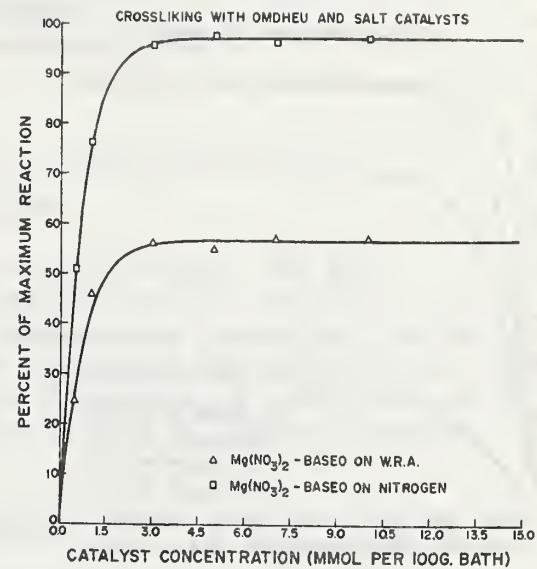


Figure 2

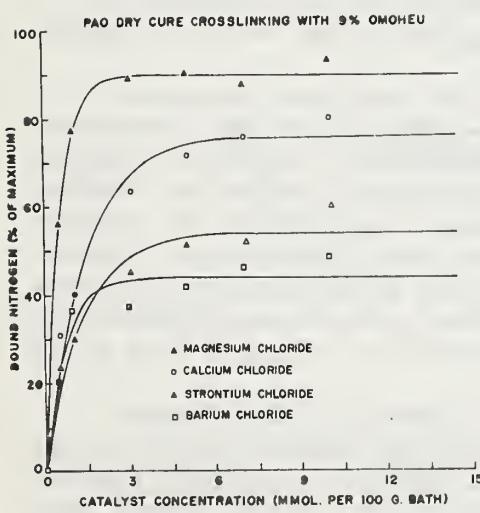


Figure 3

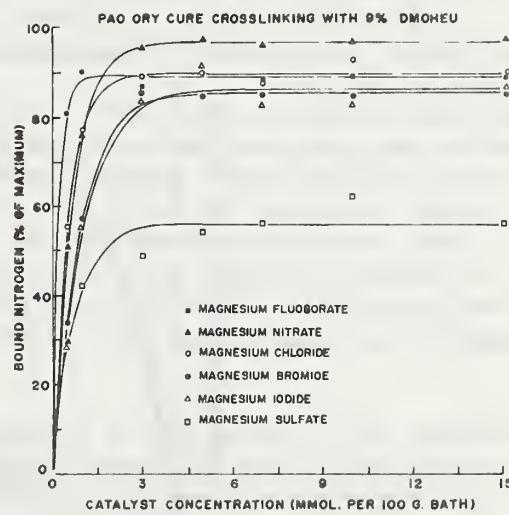


Figure 4

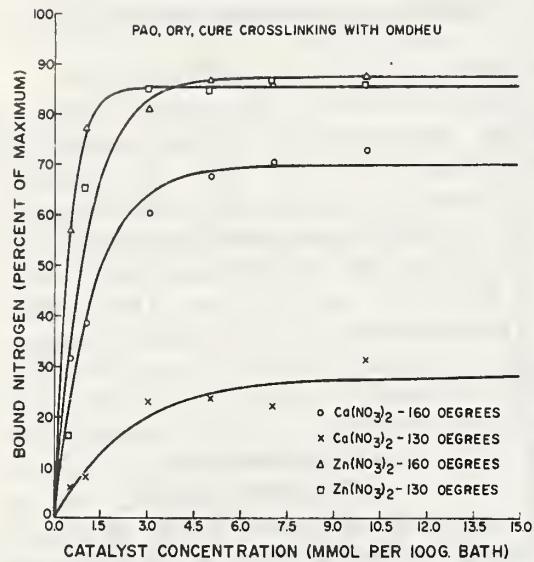


Figure 5

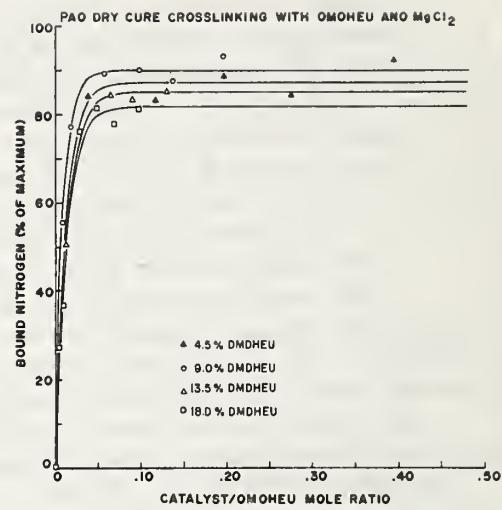


Figure 6

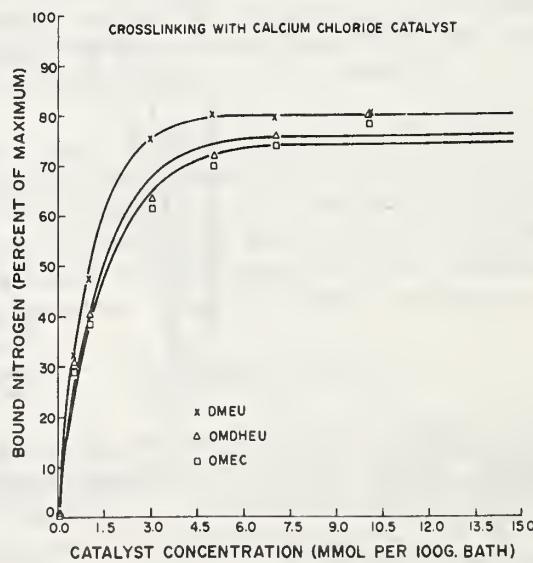


Figure 7

## PROGRESS REPORT ON FUNGICIDES TO REPLACE MERCURY SERIES

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## INTRODUCTION

Because of the concern over mercury in the ecology, and the Environmental Protection Agency (EPA) investigating the industrial utility of mercury and mercury compounds, mercury-containing fungicides for textiles came under investigation. In order to compare the efficiency of non-mercury fungicides with mercury-containing fungicides, a series of evaluations were started in May of 1973, with the object of finding suitable mercury fungicide replacements.

## EXPERIMENTAL

Various non-mercury and mercury-containing fungicides known in the trade, were selected for comparative evaluations by weathering. Using conventional add-on levels as guidelines, the test fungicides were applied to plain "Pearl Gray" dyed duck to give conventional and higher than conventional add-ons. The fungicidal treated samples were only wax finished in one instance, and termed "Uncoated." The wax finished and "standard acrylic coated" samples were termed "Coated." The uncoated samples were finished with 3.77% paraffin, while the coated samples were treated with 1.26% paraffin and the "standard acrylic coating." Some samples were prepared in the SRRC pilot plant, while others were prepared by industry.

Exposures were made in three locations: Tombstone, Arizona; Knoxville, Tennessee; and New Orleans, Louisiana. The Tombstone exposures would reflect actinic (sunlight) degradation, those in New Orleans would reflect both actinic and mildew (humidity) degradation, and those in Knoxville would reflect an intermediate moderate actinic and mildew degradation. This would be less severe than the New Orleans area. The complete exposure period of evaluation is designed for 36 months (3 years), with warp breaking strength evaluations and visual mildew ratings being made and averaged after each 6 months of weathering.

Comparative performance evaluations, with all treatments and controls, are based on "Percent Retained Warp Breaking Strength" and "Visual Mildew Ratings from 0-5." Although these evaluations are being determined with each sample in each of the three locations, the average retained strength and mildew ratings, based on the three locations, are being used to rate the samples relative to acceptable performance - or failure.

The following guidelines are used to determine the status of each sample:

(A) Average Three Location Percent Retained Strength for each six months of exposure, must exceed 20% of the original fabric warp strength, before exposure, to be considered satisfactory and not failing. Values of 20%, or lower, will constitute "failure."

(B) Average Three Location Excessive Mildew Growths for each six (6) months of exposure, must not average a rating of 3 or higher (5 being maximum) for further competitive evaluation. Mildew readings averaging 3 or higher will constitute "failure."

Types of Fungicides and Controls  
(Evaluation Series)

Mercury Containing:

Phenylmercury Triethanolamine Lactate (SRRC Pilot Plant)  
Phenylmercury (Alkanolamine) Propionate (SRRC Pilot Plant)  
Commercial Mercury-Treated Samples (Submitted)

Copper Containing:

Copper Carbonate-Zirconyl Ammonium Carbonate (Cu-Zr) (SRRC Developed)  
Copper 8-Quinolinolate (Cu-8) (SRRC Pilot Plant)

Organic Sulfur Containing:

Thiazolyl benzimidazole Type (SRRC Pilot Plant)  
Alkyl isothiazolin - one type (SRRC Pilot Plant)

Chlorinated Phenolic Containing:

Dihydroxydichlorodiphenylmethane Type (SRRC Pilot Plant)

Quaternary Naphthenate Containing:

Dodecyldimethylbenzyl ammonium Type (SRRC Pilot Plant)  
Other Alkyl ammonium Types (SRRC Pilot Plant)

Pentachlorophenyl Laurates Containing (PCPL):

Pentachlorophenyl Laurate-Wax Emulsion (SRRC Pilot Plant)  
Pentachlorophenyl Laurate Emulsion Types (SRRC Pilot Plant)  
Commercial PCPL-Treated Types (Submitted)

Unknown Mercury Replacement Containing:

Mercury Substitutes (Submitted)

Controls:

Plain Pearl Gray Dyed Duck (Commercial)  
Plain Scoured Duck (Commercial)  
Plain Greige Duck (Commercial)

In the exposure series, numbers were assigned the samples, and the "coated" samples were marked with the series number followed by "C."

## RESULTS

Condition of Samples and Controls After 18 Months' Exposure. After 18 months' exposure of the "uncoated" samples and controls, the SRRC treated mercury samples show an average of 50% retained strength with 2<sup>+</sup> mildew rating. The commercial "uncoated" mercury-treated samples show an average of 50% retained strength with 0<sup>+</sup> mildew rating. The "uncoated" Cu-Zr (SRRC developed) samples show an average of 69% retained strength, and 0 mildew rating. One "uncoated" Cu-Zr sample, with only 0.28% Cu, shows 72% retained strength with 0 mildew rating. All of the "uncoated" organic treatments average 53% to 58% retained strength with 1 to 2<sup>+</sup> mildew ratings. The best "uncoated" Cu-8 treatment shows 63% retained strength with 2<sup>+</sup> mildew rating. Uncoated scoured and greige duck controls "failed" in 12 to 18 months, while the uncoated Pearl Gray dyed duck control shows 55% retained strength with 2<sup>+</sup> mildew rating (near failure in 18 months). One thiazolyl benzimidazole sample (uncoated) failed with a 3 mildew rating.

After 18 months' exposure of the "coated" samples and controls, the SRRC treated mercury samples show an average of 65% retained strength with 0<sup>+</sup> mildew rating. The commercial treated mercury samples (coated) show an average of 74% retained strength with 0<sup>+</sup> mildew rating. The coated Cu-Zr (SRRC developed) samples show an average of 75% retained strength with 0 mildew rating. All of the "coated" organic fungicides average 61% to 77% retained strength with 0<sup>+</sup> to 2<sup>+</sup> mildew ratings. The best coated Cu-8 treatment shows 71% retained strength with 1<sup>+</sup> mildew rating. One "coated" alkyl isothiazolin-one sample shows 78% retained strength with 0<sup>+</sup> mildew rating. The best chlorinated phenol treatment shows 77% retained strength with 1<sup>+</sup> mildew rating. The best quaternary treatment shows 77% retained strength with 0<sup>+</sup> mildew rating. The best PCPL treatment (coated) shows 70% retained strength with 0<sup>+</sup> mildew rating. Only one Pearl Gray dyed duck (coated) control remains with 65% retained strength and 0<sup>+</sup> mildew rating. Coated scoured and greige duck controls failed in 12 to 18 months.

After 18 months of exposure, it is still too early to draw final conclusions.

## ANTIBACTERIAL FINISHING OF COTTON-PROSPECTS AND POSSIBILITIES

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## INTRODUCTION

Although the concept of protecting clothing from microorganisms dates back to ancient times, the idea of finishing textiles to make them resistant to bacteria or capable of killing bacteria on their surface has only received sporadic attention in the last twenty years. Considering the market possibilities, specifically those in which cotton could be utilized, and intensive research effort in this area appears to be worthwhile. Consumption of all fibers in the United States in 1973 amounted to 9,218.5 million pounds, of which 2,694.1 was cotton (29.2% of the total)<sup>1</sup>. Specific end-uses in which cotton could be employed for antibacterial finishing are listed in Table I. In addition to the specialty medical field and sanitary uses, this type of finishing could be applied to all types of apparel, sheets, towels, and bedspreads, as well as underwear and hosiery. The total current consumption of the cotton fiber based on these end-uses alone is a sizeable 2,304 million pounds.

In dealing with finishing applications based on this concept, the scope of treatments to be considered are those utilizing antibacterial and antiviral agents; this can be further subdivided into bacteriostatic agents (those capable of inhibiting new bacterial growth) and bactericides and virucides (those capable of killing bacteria and viruses which come into contact with the cotton textile). Areas of application to be excluded from consideration are the well-documented antifungal, mildew and rot-proofing, and aligicidal finishing of textiles as well as their disinfection, which involves removal of already present bacteria and viruses as opposed to initial prevention of their presence on cotton textiles.

## PRACTICAL CONSIDERATIONS

Naturally, the end-use of the cotton textiles will dictate which bacteria and viruses are either to be inhibited in their growth or killed by the action of antibacterial and/or antiviral agents. It has been found, for example, that S. epidermidis and Corynebacterium sp. are the most prevalent bacteria which cause body perspiration odor<sup>2</sup>; correspondingly, fabrics used for apparel, underwear, and hosiery, would have to either be bacteriostatic or bactericidal towards these bacteria to be useful in suppressing or preventing odor development in the fabrics. Conversely, fabrics used in medical and sanitary applications, as well as fabrics used for sheets, bedspreads, and towels in hotels, hospitals, and other public institutions, would have to be effective against such bacteria as S. aureus, E. coli, Str. pyogenes, bacillus spore formers, and common pathogenic viruses such as polio and influenza.

Important characteristics of antibacterial and antiviral agents, some of which have been discussed by Gagliardi<sup>3</sup>, are: (1) toxicity, (2) durability, (3) compatibility, (4) selectivity, and (5) marketability. Toxicity includes that of the reagent before application to the fiber, adverse effects of the reagent as a water or air pollutant, and any adsorption or dermatitis problem the reagent could cause when the fiber contacts the human skin. Durability requirements will vary widely with the end-use of the cotton textile, and should be realistically assessed in each specific area of application. Compatibility of the antibacterial or antiviral agents with other finishing agents such as durable press resins and flame retardants, may be desirable in certain instances, and should be taken into consideration. The effects, either beneficial or harmful, which the antibacterial finish produces on subsequent dyeing processes, should be carefully evaluated. As previously mentioned, selectivity will depend on which bacteria are most problematic for the specific textile end-use. Marketability will be gauged by the cost of finishing the cotton textiles relative to the desirable antibacterial and antiviral effects produced in the fabrics or fibers.

There are literally thousands of chemicals listed as antibacterial and antiviral agents, most of which are reported in the biological literature. Gagliardi<sup>3</sup> has discussed at length, various classes of potential antibacterial agents, most of which are based on the controlled slow release of the chemical agent from the fiber. However, it is also theoretically possible to produce an inherently biostatic cotton fiber by polymerization of appropriate monomers on the fabric. Some of the more frequently reported antibacterial and antiviral agents are phenols, onium salts, iodine and iodophors, antibiotics, nitro and halogen compounds, sulfa drugs, various metal salts, organometallics, carbanilides, and many other types of chemical agents.

#### CURRENT AND FUTURE RESEARCH

The current state of the art in antibacterial finishing is generally that of piecemeal efforts and superficial evaluations. One of the major problems is the lack of choice of test methods for a realistic appraisal of antibacterial finishes. Of the tests listed in the most recent AATCC manual<sup>4</sup>, only the Quinn test gives a quantitative measurement of bacteriostatic or bactericidal effectiveness. This test has the advantage of measuring the antibacterial activity of the fabric directly, but the disadvantage is that it is time consuming and expensive to conduct. Most qualitative tests measure the antibacterial activity of the fabric indirectly by diffusion of the chemical agent from the fiber into an agar medium. More tests, particularly quantitative ones, relating antibacterial activity to fiber end-use, are needed. Increasing interdisciplinary efforts between microbiologist and textile chemists would certainly improve this situation.

Present terminology, both in relation to durability and selectivity of antibacterial agents to appropriate fiber end-uses, is used rather

loosely and in many cases, causes misconceptions and semantic difficulties. Future publications should strive to be explicit in their terminology to ensure correct interpretation of the scope of the antibacterial finish as well as a realistic definition of its durability. Additional progress in this field may be achieved by investigating the -static and -cidal effects of chemical agents on specific bacteria of interest as well as elucidating and explaining any synergistic or antagonistic antibacterial agent relationships. Other interesting areas of research which should be explored include a determination of the rate of removal of antibacterial agents from the fiber under normal and simulated end-use conditions, ascertaining the most effective mode of action of antibacterial agents on the cotton fiber, and closely relating antibacterial activity to fiber end-use.

Preliminary efforts in our research focus on evaluating various chemical reagents as bacteriostats and bactericides by the parallel streak test (using S. aureus and E. coli as representative pathogenic organisms) and the Quinn test (with S. epidermidis as the representative odor-producing bacteria). Results of selected treatments are shown in Table II. Chloro-deoxycellulose and thiocyanatodeoxycellulose fabrics<sup>5</sup> (unlaundered) are moderately effective in the parallel streak test, but are ineffective in inhibiting growth of S. epidermidis. Conversely, the zirconium acetate-hydrogen peroxide treatment, which is believed to deposit a crosslinked insoluble peroxidic polymer on the cotton fiber<sup>6</sup>, is 100% effective as a bacteriostat for S. epidermidis, although it is only moderately effective in the parallel streak test. Cellulose sulfite fabric, prepared by reaction of native cotton with thionyl bromide in DMF<sup>7</sup>, is quite good in both tests, giving a 2 mm. zone of inhibition in the parallel streak test (P<sup>+2</sup>) and 100% bacteriostasis by the Quinn test. The zirconium acetate-dichlorophene treatment, based on previous work of these complexes as fungicides<sup>8</sup>, is likewise very effective in both tests. It gives a zone of inhibition of 8 mm. in the parallel streak test (P<sup>+8</sup>) and 100% inhibition of S. epidermidis. All of the data reported here have been on samples washed in hot water after their finishing treatment, but unlaundered. Laundering studies are in progress to determine the durability of these finishes under carefully controlled conditions relating to their end uses.

#### SUMMARY

Antibacterial finishing for cotton textiles, if researched and developed in an intelligent and discerning manner, should produce large new markets for fiber consumption. A wide variety of finishes are needed having varying requirements for aesthetic as well as health uses. The characteristics of representative bacteria and chemical reagents should be carefully examined. Many opportunities for research now exist in this field, some of which are currently being explored at the Southern Regional Research Center of the USDA, ARS.

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## ENERGETICS AND MECHANISMS OF THERMALLY INITIATED FREE RADICAL OXIDATION OF COTTON AS RELATED TO FLAME RETARDANCY

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### INTRODUCTION

Studies of reaction mechanisms of thermally initiated oxidative degradation of cellulose have involved the use of thermogravimetric and differential thermogravimetric analyses, differential scanning calorimetry, and chromatographic methods for determining the products derived from heated celluloses<sup>1</sup>. Practical methods of altering the oxidative processes of thermally initiated reactions of cellulose, with the objective of preparing flame- and glow-resistant cotton products, have been reported. Theories proposed to explain the mechanisms by which the oxidative processes are altered to yield flame- and glow-resistant products have been divided into five categories: coating, gas, thermal, hydrogen bonding, and dehydration<sup>2</sup>. Most of these studies have involved reactions of cellulose at temperatures ranging from about 300° to 600° C. in which measurable changes in composition and weight losses occurred.

Electron spin resonance (ESR) spectroscopy provides a more sensitive method for detecting thermally initiated reactions of cellulose than the methods listed above<sup>3-7</sup>. This report describes the application of ESR spectroscopy to the study of thermally initiated oxidative reactions of cellulose. The effects of experimental conditions on the oxidative degradation of cellulose by processes of depolymerization to yield products with reactive, short-lived free radicals or by processes of decomposition of anhydroglucosidic units to yield products with unreactive, long-lived free radicals are discussed. The effects of temperatures at which the products of the latter reactions yield chars with different reactivities with oxygen are discussed.

### EXPERIMENTAL

Cotton cellulose of the Deltapine variety was purified in the usual manner<sup>8</sup>. After conditioning the cellulose at 21° C. and 65% RH, the resulting product had a moisture content of about 7% and a viscosity-average molecular weight of about 700,000<sup>9</sup>. Thermally initiated free radicals in cotton cellulose at temperatures ranging to 300° C. were produced and evaluated in a Varian 4502-15 EPR spectrometer system<sup>10</sup> equipped with a variable temperature accessory. Free radicals in cotton chars formed at temperatures greater than about 300° C. were formed externally and then transferred into the spectrometer for evaluation. Some cotton samples were soaked in chemical solutions and then padded and dried in vacuum over P<sub>2</sub>O<sub>5</sub> at 25° C. for at least 16 hr. prior to packing the treated cotton into the ESR sample tubes for heating. Chemicals used were reagent grade.

## RESULTS AND DISCUSSION

Energy of Activation. Energies of activation ( $E_A$ ) for thermally initiated degradative reactions of cellulose are summarized in Table I. The values were calculated from Arrhenius plots, based on weight-loss or ESR free-radical determinations. When volatile degradation products were evacuated, as they were formed in degraded cellulose,  $E_A$  for thermal degradation for purified cellulose I were 50 and 53 kcal-mole<sup>-1</sup>, determined by weight-loss or ESR, respectively.  $E_A$  for thermal degradation of cellulose was almost independent of cellulose crystal lattice type, degree of crystallinity, and molecular weight of cellulose. For example, values for hydrocellulose I, prepared from cellulose I by HCl hydrolysis, or cellulose II were 47 and 49 kcal-mole<sup>-1</sup>, respectively. When purified cellulose I was heated in nitrogen under static conditions,  $E_A$  for thermal degradation was decreased to 33 kcal-mole<sup>-1</sup>. Evidently, the presence of breakdown products catalyzed the thermal degradation of cellulose.

When cellulose I that contained NaCl was heated,  $E_A$  for thermal degradation was reduced to about 35 kcal-mole<sup>-1</sup>. When cellulose I that contained Na<sub>2</sub>CO<sub>3</sub> or sodium acetate buffer (pH 5) was heated,  $E_A$  was reduced to 19 kcal-mole<sup>-1</sup>. However, for the case of Na<sub>2</sub>CO<sub>3</sub>, evidently there was a lattice type effect. For example, when cellulose II that contained Na<sub>2</sub>CO<sub>3</sub> was heated,  $E_A$  was reduced to only 30 kcal-mole<sup>-1</sup>. Similar effects on  $E_A$  were recorded when NaHCO<sub>3</sub>, KHCO<sub>3</sub>, boric acid, borax, and monopotassium phosphate were added to cellulose before heating.

ESR Spectra. Typical singlet ESR spectra for chars derived from cellulose I and cellulose II, heated at 300° C. with continuous evacuation of volatile degradation products, are described in Table II. Free radicals in the chars are resonance stabilized; for example, these radicals do not initiate polymerization of vinyl monomers. When the spectra were recorded with the chars exposed to air, there was an increase in both apparent free-radical concentration and line width. The g-value's for the spectra were increased slightly on exposure of the chars to air. The ESR spectra of chars from both cellulose I and II had about the same characteristics.

Char Formation. The free-radical concentrations in the chars increased as the temperature of char formation increased from about 200° C. to about 560° C., as shown in Tables III and IV. At temperatures of about 620° C., there was a sharp decrease in free-radical concentration. Chars formed at temperatures greater than 340° C. reacted with oxygen to give a decrease in free-radical concentration. However, when oxygen was removed, an increase in free-radical concentration occurred. Chars formed at temperatures less than 340° C. reacted with oxygen to give an increase in free-radical concentration. When cellulose was treated with an additive before char formation, this effect was further increased, after reaction of the char with oxygen, as shown in Table IV.

## CONCLUSIONS

Thermally initiated degradation of cotton cellulose evidently follows an oxidative depolymerization route and/or a carbonization route with dehydration of cellobiose units, as follows:

### oxidative depolymerization



### carbonization



Oxidative degradation of cotton cellulose that preponderantly follows the depolymerization route (equations 1 and 2) results in evolution of heat that increases the rate of oxidation of cellulose, leading to flaming or glowing of cotton even after the source of heat is removed. Oxidative degradation of cotton cellulose that preponderantly follows the carbonization route (equation 3) results in little or no evolution of heat, so that the rate of oxidation of cellulose does not increase; after the source of heat is removed, there is less tendency for flaming and/or glowing of cotton. Electron spin resonance spectroscopy was used to follow selectively the carbonization route. Carbonization leads to formation of carbon radical ring structures that are resonance stabilized; depolymerization leads to formation of short-lived free radicals<sup>7,12</sup>.

Additives on cotton cellulose decreased the energy of activation of carbonization. ESR detectable free-radical concentration in chars that were formed at temperatures about the decomposition temperature of cellulose increased on contact with oxygen. ESR detectable free-radical concentration of chars that were formed at temperatures greater than the decomposition temperature to about the ignition temperature of cellulose decreased on contact with oxygen. Chars formed at temperatures about the ignition temperature of cellulose contained low concentrations of ESR detectable radicals. These effects indicate the extent and nature of carbonization of cotton: formation of carbon ring structures in slightly interacting chars at lower temperatures to formation of carbon ring structures in highly interacting or crosslinked chars at higher temperatures. The oxygen diradical reacts with free radicals in carbon ring structures that are in slightly interacting chars, further opening the char layers to decrease the orbital interactions between other free radicals thereby yielding an increase in ESR detectable radicals. Oxygen reacts reversibly

with pendant free radicals in carbon ring structures in highly interacting chars, broadening the line widths of the spectra, thereby yielding a decrease in ESR detectable radicals.

Treatments that lead to thermally initiated degradation of cotton cellulose to form crosslinked carbon ring structures should minimize further oxidation of cotton after the source of heat is removed. This should result in preparation of cottons that are flame and glow resistant.

## FIRE-RETARDANT COTTON/MODACRYLIC KNIT FABRICS

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Conventional methods of treating cotton apparel fabrics to impart flame retardancy consist of using phosphorus-containing compounds or polymers. Garments made from fabric so treated remain flame retardant after 50 or more launderings. One shortcoming is that some treatments fail when the garments are laundered with chlorine bleach. It is thought that the bleach breaks down the phosphorus-nitrogen polymer complex which is the basis of the flame retardancy and thus flame resistance is gradually lost.

Some flame retardants for outdoor fabrics are based on the synergistic effect of halogen and antimony oxide. It was speculated that inherently flame-retardant modacrylic fibers that contain relatively large quantities of halogen would suffice as a halogen source when used in blends with cotton. The plan was to treat fabric blends of cotton and modacrylic fibers with an N-methylol resin to bind antimony oxide in the fabric and to impart weather resistance and/or durable-press properties depending upon the end use of the product. Early screening experiments were carried out by determining flame-resistance characteristics of small pads consisting of blends of cotton and modacrylic fibers. The small pads were tested by an oxygen index (OI) technique.

This paper reports preliminary work to produce flame-retardant knitted fabrics that would be suitable for children's sleepwear and whose fire retardancy is not adversely affected by chlorine bleach in laundering.

Initial resin treatment on small experimental fabrics of 85/15 and 70/30 cotton/modacrylic fibers resulted in surprisingly high OI values by resin treatment alone. These values were further enhanced when antimony oxide as flame-retardant additive was used in the resin formulation.

Larger samples of both flat knit and tubular knit fabrics were prepared. The flat knits were 6.8 oz./sq. yd., and the tubular knits were 6.0 oz./sq. yd. Fiber ratios in both knits were 83/17 and 67/33 cotton/modacrylic, respectively. The study was expanded to include intimate and mixed blend fabrics. Fabrics that consisted of yarns of a single composition (uniformly blended fibers) were considered as intimate blends. Those that were prepared from more than one type of yarn in blend composition were considered mixed blends.

Both types of these knitted fabrics in each blend ratio were treated with a formulation consisting of 17% trimethylolmelamine and 5% antimony oxide. This formulation was used in an effort to produce a predominantly cotton flame-retardant product within a reasonable price structure. They were evaluated for flame retardancy by the DOC FF 3-71 test after 50 wash cycles using 90 gms. of AATCC detergent and with and without 9 ozs. of sodium hypochlorite bleach in each laundry cycle. Some fabrics of all weights and blend ratios passed the DOC test after 50 wash cycles. Highest char length values were for the 83/17 cotton/modacrylic mixed blends. This type blend for the 83/17 cotton/modacrylic is close to the lower limits of modacrylic content for flame retardancy when 5% of antimony oxide is used.

All treated samples showed a significant loss of bursting strength after laundering with bleach indicating that the hypochlorite reacted with the melamine resin and the resultant product attacked the cellulose, probably during the tumble drying that was part of each wash cycle. Samples most affected were those containing some all-cotton yarns. Also noted was that intimate blends with larger amounts of modacrylic fiber are more chlorine resistant than those with lower contents.

Experiments using a vinyl chloride-vinylidene chloride copolymer as an additional source of halogen and binder for antimony oxide resulted in the highest oxygen index value of flame retardancy in this fabric blend study. Use of this copolymer should permit the use of less of the trimethylol melamine and thus produce treated fabrics which lose less strength when laundered with bleach.

On the basis of oxygen index tests and the DOC Flammability Test, evidence has been presented to show that low levels of inherently flame-retardant polymers in fibrous form may be blended with cotton to produce flame-retardant fabric. These knit fabrics could be used for children's sleepwear as they are flame retardant before and after 50 DOC-type laundry cycles. Use of chlorine bleach does not significantly reduce flame retardancy although strength properties of treated fabrics is lowered.

## TOPPING OF THE THPOH-NH<sub>3</sub> FIRE-RETARDANT FINISH

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### INTRODUCTION

Since the discovery of the THPOH-NH<sub>3</sub> process (1) at SRRC (and its disclosure at the 7th annual conference in 1967), it has been the subject of numerous research and development projects. Improvements and variations in the process have resulted from this continuing research effort. At least three commercial processes are presently in use, particularly in the flameproofing of cotton flannelette for children's sleepwear. The particular advantages of the process are development of durable flame-retardance properties with little or no loss in breaking strength or change in hand.

Our present work in this general area began with a number of unsuccessful attempts to perform the process by a simple pad-dry-cure procedure, i.e., curing was attempted without an ammonia chamber. Later some success was achieved by heat curing an ammonia-urea-formaldehyde precondensate (2) with partially-neutralized tetrakis-(hydroxymethyl)phosphonium chloride (Thpc). Treated cotton flannelette fabrics, with original wrinkle-recovery angles up to 286°, passed the DOC FF 3-71, but fabric strengths were reduced (40-50% tear strength retained) to the point that there appeared to be no distinct advantage (other than the wrinkle resistance properties) over other Thpc-amide (3) finishes. The precondensate contained a 5:5:2+ molar ratio of urea:formaldehyde:ammonia and was prepared by the slow addition, with cooling, of ammonium hydroxide to an aqueous solution of the other reactants. A typical formulation (pH=6.5, for flameproofing cotton flannelette was as follows:

Thpc-----	19%
Precondensate---	9%
Na <sub>2</sub> HPO <sub>4</sub> -----	3.8%

The central idea behind our attempts to improve the THPOH-NH<sub>3</sub> finish by combining it with a second finish was to reduce the average length of the polymer chains and thereby reduce stiffness and tearing strength losses. Presumably, the shorter length polymers would be less able to bind the fibers together. Whereas, this effect was not achieved in the fabric treatments with the aforementioned precondensate, we were able to achieve high phosphorus and nitrogen levels on cotton, generally without stiffness and excessive loss of strength, by topping a low level THPOH-NH<sub>3</sub> finish with THPOH-amide (4) or Thpc-urea finishes (3) which provided a simple method for upgrading marginal or unsatisfactory flame-retardant fabrics.

The variables in a study of this type are numerous. For a major part of the work, four base fabrics (flannelette) were used. These fabrics had been treated with various levels of THPOH-NH<sub>3</sub> and oxidized

with hydrogen peroxide (5). Pad-bath solutions of 25 and 28% THPOH were used to produce marginal finishes; whereas, pad-bath solutions of 20 and 24% THPOH produced fabric which often burned after less than 15 launderings. Formaldehyde odor is relatively low in these treatments, because of the lower THPOH concentrations.

A number of different formulations were used for the second or topping treatment - including some which contained no phosphorus compounds. The combined treatments which produced durable flame-retardant fabrics were those wherein the solids content from the nitrogen and phosphorus-containing components of the first pad bath plus the solids content from the second pad generally added up to at least 35-36%. The following formulations are typical for the pad baths used in the topping experiments:

1. 2.5-4% Trimethylolmelamine (TMM),  $MgCl_2$ , catalyst
2. 3% Dimethyloldihydroxyethyleneurea (DMDHEU),  $Zn(NO_3)_2$  catalyst
3. 1.2% Urea, 0.6%  $Na_2HPO_4$ , 3.8% Thpc
4. 2.4% Urea, 1.1%  $Na_2HPO_4$ , 7.6% Thpc
5. 1% Urea, 0.7% TMM, 3.3% THPOH
6. 4% Urea, 2.8% TMM, 13.3% THPOH

A total of 43 fabrics (including the base fabrics) were prepared as described above, tested for textile properties, analyzed for nitrogen and phosphorus contents, and examined for durability of flame-resistance properties through 50-laundry cycles. One of the marginal base fabrics and 18 of the topped fabrics were flame retardant after the laundry cycles. As noted previously, a combined pad-bath solids content of 35-36% was generally required. Stiffness was a problem with only one of the topped fabrics. The topping treatment had little or no effect upon the wet wrinkle recovery of the fabric, but dry recovery was generally improved 30-40%.

The topping treatment caused a loss of 25-67% in breaking strength, but most of losses were 25-30% for the urea-TMM-THPOH aftertreatment and 35-55% for the urea- $Na_2HPO_4$ -Thpc aftertreatment. Losses in tearing strength followed the same sequence but were of lower magnitude.

Topping with urea-TMM-THPOH produced a relatively large increase in phosphorus content compared to the increase in nitrogen. Further experimentation demonstrated that THPOH reacted directly with the oxidized THPOH- $NH_3$  polymer as well as with the amides present in the pad bath.

Topping of unoxidized THPOH- $NH_3$  treated fabrics was also studied. The disadvantages of this variation are color formation which may not be totally removed by a "final" hydrogen peroxide bleach, possible precipitation in the second pad bath caused by ammonia in the fabric, loss of some phosphorus from the unoxidized fabric into the second pad bath, and a greater stiffness problem. The experience to date suggests that oxidation before topping is preferred.

Additional topping treatments have been performed on oxidized THPOH- $NH_3$  cotton twill for the purpose of determining the effects of a second treatment with TMM or DMDHEU on durable-press ratings and

resistance to chlorine bleach. The durable-press ratings are improved somewhat by the second treatment, but not as much as an untreated fabric is improved by the same treatments. Topping produced a small improvement in the resistance of the flame retardance properties to chlorine bleach.

In summary, phosphorus and/or nitrogen contents of a THPOH-NH<sub>3</sub> treated fabric can be increased by a second or topping pad-dry-cure treatment without adversely affecting the hand of the fabric. The major advantage to be obtained by a topping treatment is the upgrading of a marginal or unsatisfactory THPOH-NH<sub>3</sub> flame-retardant fabric.

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## TRANSFER TECHNIQUES FOR PRODUCING FLAME-RETARDANT COTTON FABRICS

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### INTRODUCTION

The THPOH-NH<sub>3</sub> finish is one of the most widely used flame retardant finishes for cotton fabric. The process currently being used in finishing mills employs an ammonia gas cure. Wider commercialization of this finish would probably be achieved if conventional pad bath curing techniques could be employed; however, conventional padding of THPOH-sensitized cotton fabric through ammonium hydroxide solutions causes polymer to slough off in the pad bath and on the pad rolls, resulting in very little polymer being fixed on the fabric. This paper examines several transfer padding techniques in which limited quantities of various ammonia donors are transferred to THPOH-sensitized fabric.

### EXPERIMENTAL

The fabric used in this study was a 5.0 oz./sq. yd. cotton flannelette which had been scoured to remove napping oils. A 35% active solids solution of THPOH was used in all of the work reported in this paper. Initial padding of fabric with THPOH was carried out using either a conventional two-roll pad or vacuum impregnation. For curing of the THPOH-sensitized fabric, a three-roll Benz padder was used which permitted continuous loop operation in which excess padding solution could be squeezed off prior to the actual solution transfer from the loop to the sensitized fabric. Another Benz two-roll padder was used for loop operation, but in this case excess solution was removed by wiping the loop continuously with a doctor blade or round metal bar. In addition to the two loop methods mentioned above, a conventional two-roll padder equipped with a steel bottom roller and a rubber top roller was adjusted so that the bottom roller turned in the padding solution and acted as a kiss roll. Single passes through the three-roll pad gave wet pickups of from 5-40%, through the two-roll pad of from 40% to 70%, and over the kiss roll of from 15-40%. All cured fabrics were process-washed, peroxide oxidized, washed and dried in the conventional way.

## RESULTS

Various methods of transfer padding ammonium hydroxide or aqueous ammonium salt solutions onto THPOH-sensitized cotton flannelette have been investigated. These include the use of fabric loops on two- and three-roll padders, and the use of a liquor or kiss roll. Although all of the methods used were effective to some degree, the use of a fabric loop on the three-roll pad followed by drying then finally by either quenching in ammonium hydroxide or by using an ammonium hydroxide loop transfer on a two-roll pad seems to produce consistently the best and most even results.

There appears to be a definite advantage to limiting the amount of water which is transferred to the THPOH-sensitized fabric during the initial curing step. This is most easily accomplished through the use of either the loop method on a three-roll pad or a kiss roll method. In either case, a concentrated solution of the ammonia donor should be used. After the phosphorus-nitrogen polymer is initially fixed, efficiency can be improved by a final ammonium hydroxide treatment on either the two- or three-roll pads using a fabric loop, on a kiss roll, or simply by immersion. A drying step between the initial fixation step and the final curing step is desirable for maximum efficiency, but is not required.

Polymer fixation and durability of the finish to laundering is further improved by the addition of hexamine to the ammonium hydroxide curing bath. This modification is recommended whenever lower than normal levels of THPOH are being applied to cotton fabric or when the speed of curing must be increased. Anhydrous liquid ammonia also has been used quite effectively as a curing agent when it is employed in one of the transfer curing systems.

## CONCLUSION

Several methods for the transfer pad curing of THPOH-sensitized cotton flannelette with various ammonia donors have been used to produce fire retardant flannelette samples which were durable to fifty standard launderings. With aqueous curing agents, minimizing the amount of water transferred during the initial cure, use of a drying step between the initial cure and the final cure, and the incorporation of hexamine into the ammonium hydroxide pad baths have all increased polymer fixation efficiency. Use of a modified pad method, with either aqueous ammonia donors or with liquid ammonia as described in this paper should greatly increase the speed of processing of THPOH-NH<sub>3</sub>-treated fabric.

## IMPARTING FLAME RETARDANCY TO COTTON BLENDs USING THPOH-NH<sub>3</sub>

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### INTRODUCTION

The THPOH-NH<sub>3</sub> process is a well known method for imparting durable flame retardance to 100% cotton fabrics. Since the Flammable Fabrics Act was amended in 1967, this process has been the subject of increased investigations designed to obtain durable flame retardancy. It is now a commercialized process for woven as well as knit fabrics. Likewise, chemical finishing of 100% polyester fabrics for obtaining durable flame retardancy has received much attention. The use of brominated compounds, such as tris-2,3-dibromopropyl phosphate, is the most significant commercial method for treating 100% polyester fabrics.

However, the chemical finishing of cotton/polyester blends for imparting durable flame retardancy is still in the developmental stage and is the subject of this investigation. Our objective was to examine the limitations of the THPOH-NH<sub>3</sub> finish on cotton blends of various compositions, and/or constructions.

### EXPERIMENTAL

THPOH was prepared by slowly adding 25% NaOH (0.6 moles) to dilute Thpc (1.0 moles) to pH of 7. Wetting agent (0.2% Triton X-100) was added and the remaining water added to give a stock solution of 40% THPOH. Pad baths of lower concentrations were obtained by dilution of the stock solution. Fabric samples (12" x 60") were treated in the laboratory by padding through THPOH solution using 2 dips and 2 nips at 60 p.s.i. pressure. The samples were dried at 85°C for 5 minutes (fabrics G & H dried for 4 minutes), cured by exposure to NH<sub>3</sub> gas for 5 minutes then oxidized in 2% H<sub>2</sub>O<sub>2</sub> for 2 minutes. The fabrics were given a process wash in a washing machine without detergent, tumble dried and allowed to equilibrate. The samples were weighed and the percent add-on (% A.O.) determined.

A description of sixteen fabrics used in the evaluation is shown in Table I. Each fabric was treated with THPOH-NH<sub>3</sub> at various levels of percent add-on then evaluated for the following data:

- (1) Breaking strength, (bursting strength for knits);
- (2) Tearing strength;
- (3) Stiffness;
- (4) Percent phosphorus;
- (5) Percent nitrogen;

- (6) Oxygen Index (OI);
- (7) Flammability Test DOC FF 3-71;
- (8) Test 4, 5, 6, 7 after 25 and 50 home laundry cycles.

## RESULTS AND DISCUSSION

The breaking strength retention or bursting strength retention of almost all treated fabrics was near 100%. An average of approximately 60% tearing strength retention was obtained for all treated fabrics tested in both warp and fill directions.

Stiffness values in warp and fill were used as an indication of the hand of the treated fabric. Most stiffness values were in a tolerable range considering that no softener was used in the formulation.

The difficulty of treating cotton blends for obtaining durable flame retardancy is exemplified in Table II. Referring back to Table I, it is noted that the samples within the three sets of fabrics in Table II have identical constructions. The only variable is % cotton and % add-on. These results show that the greater amount of cotton present in the fabric, the lesser the amount of add-on required to obtain flame retardancy. This is not surprising but it does show that it is possible to treat a 50/50 blend with THPOH-NH<sub>3</sub> to give durable flame retardancy.

It should also be noted that the OI values of treated blends are considerably lower than the OI values of treated 100% cotton even though the % add-on is much greater in the blend fabrics. However, a low OI value of a treated blend does not necessarily mean that the sample will fail the DOC test. As shown in Table II, samples of 50% cotton (K & Ø) passed DOC-50X with OI values of 27.0 and 26.5 whereas 100% cotton samples (I & P) failed DOC-50X with OI values of 28.6 and 28.0, respectively.

Cotton/polyester blends gave better flame retardant properties than did an identical construction of cotton/nylon blends. Table III shows that the OI values of the polyester blends were higher than the corresponding nylon blends. This difference in OI values was also consistent at three other levels of % add-on for both 50% cotton blends and 70% cotton blends.

The selected samples in Tables II and III are representative of the OI values and DOC test results after 25X and 50X of all 16 fabrics treated at 3 or 4 levels of % add-on. Based on these results, the OI value could be correlated to the DOC test (pass or fail, not char length) for all fabrics tested. In general, treated blended fabrics would fail the DOC test if the OI value was < 26 and pass if OI was > 27. Treated fabrics of 100% cotton would fail the DOC test with an OI < 29 and pass with an OI > 30. OI values between these sets of figures were considered borderline.

The results of a THPOH-NH<sub>3</sub> pilot plant treatment of 20 yds full width fabric F is shown in Tables IV and V.

There was approximately 100% retention in breaking strength but approximately 50% retention in tearing strength. The treated fabric had a full hand as indicated by stiffness data. It is believed that the last two properties would be enhanced by the use of softener in the formulation. Durable flame retardancy was obtained on this fabric as shown by the data in Table V.

Attempts to treat a 50/50 blend (fabric E) in the pilot plant have not yet been successful.

#### SUMMARY

A minimum of 24% add-on is required to give durable flame retardancy to 50/50 cotton/PE blends in the fabric constructs studied. Polyester blends gave better flame retardant properties than an identical construction of nylon blends.

An OI value of approximately 30 is required to pass the DOC test for treated 100% cotton fabrics. However, an OI of approximately 27 is required for treated cotton/PE blends to pass the DOC test.

A 65/35 cotton/PE flannelette was successfully treated in the pilot plant.

#### ACKNOWLEDGMENTS

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Table I. Fabric identification.

Fabric	Description	% Cotton*	Wt. oz/yd <sup>2</sup>	Gray Construction	
				Yarn Count	Yarn Size
A	Single jersey, french tuck	100	5.0	24x25	20/1-20/1
B	" "	77	5.0	" "	" "
C	" "	65	5.1	" "	" "
D	" "	50	4.9	" "	" "
E	Flannelette-print	50	3.9	43x43	26.5/1-13/1
F	-white	65	3.6	40x44	- -
G	Sheeting-white	50	3.6	109x58	33/1-37/1
H	" "	79	3.2	78x72	33/1-35/1
I	Sheeting-white	100	3.8	64x64	25/1-25/1
J	" "	70	3.9	" "	" "
K	" "	50	3.9	" "	" "
L	Soft fill sheeting	70*	3.9	43x43	26.5/1-13/1
M	" "	50*	3.9	" "	" "
N	" "	70	3.7	" "	" "
Ø	" "	50	3.8	" "	" "
P	" "	100	3.7	" "	" "

\* All blended fabrics contain polyester except L and M which contain nylon.

Table II. 100% Cotton vs. 50/50 blend of same construction.

Fabric	% Cotton	Add-on	% DOC 50X	
			OI	50X
A	100	14	Pass	31.4
D	50	21	Fail	26.1
D	"	23	Pass	26.5
I	100	12	Fail	28.6
I	"	19	Pass	31.6
K	50	21	Fail	26.3
K	"	24	Pass	27.0
P	100	13	Fail	28.0
P	"	19	Pass	30.3
Ø	50	25	Fail	26.1
Ø	"	27	Pass	26.5

Table III. OI of polyester blend vs. nylon blend at 23% add-on.

	50% Cotton		70% Cotton	
	PE	Nylon	PE	Nylon
Orig.	26.6	25.4*	28.0	26.8
25X	26.5	25.4*	27.7	26.6
50X	26.3*	24.8*	27.9	26.5

\* Failed DOC test.

Table IV. Pilot plant treatment 65/35 cotton/PE (Fabric F).

Breaking str., lbs.	W F	Control	Treated
		28.98 37.62	28.20 40.08
Tearing str., grams	W F	2650 2900	1240 1453
Stiffness, in-lbsX10 <sup>-4</sup>	W F	1.83 1.49	13.00 5.49

Table V. Pilot plant treatment 65/35 cotton/PE (Fabric F).

P, %	Orig. 4.09	25X 3.92	50X 3.70
N, %	1.97	1.88	1.86
OI	27.1	26.6	26.3
DOC,	-	2.8	2.9
Char length, in.			

## SMOLDER-RESISTANT COTTON BATTING BY VAPOR PHASE DEPOSITION OF BORIC ACID

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## INTRODUCTION

Methyl borate is readily produced by solution of boric acid in anhydrous methanol as shown in the following reversible reaction:



The resulting methyl borate (b.p. 68°C) and excess methanol (b.p. 64°C) form a minimum boiling azeotrope (b.p. 54.6°C) which is quite volatile. Consequently large amounts of both methyl borate and methanol are present in the vapors above the solution. An excess of water reverses the reaction equilibrium by hydrolysis of the methyl borate back to methanol and boric acid. When cotton batting is exposed to the vapors the moisture present in the batting hydrolyzes the methyl borate resulting in a deposition of boric acid on the batting.

## EXPERIMENTAL

Garnetted cotton batting was suspended over a 5-liter saturated solution of boric acid and anhydrous methanol (270 gm boric acid/1000 gm solution) in a 52-liter enclosed reactor. The solution in the chamber was allowed to equilibrate for at least four hours before the cotton sample was exposed to the vapors. Variations in exposure time (1 to 120 minutes), initial moisture content of sample (0% to 12.9%), and reactor temperature (65-160° F.) were investigated to determine their effects on the amount of boric acid deposited. The samples were analyzed for boric acid content by titration with sodium hydroxide in the presence of mannitol. Several samples were constructed into mini-mattress configurations and tested according to cigarette ignition tests requirements of FF 4-72 Mattress Flammability Standard.

## RESULTS

Table I shows the results of cigarette ignition tests performed on a number of cotton batting samples treated as described above.

TABLE I  
 MINI-MATTRESS TESTS  
 $\text{MeOH-H}_3\text{BO}_3$  VAPOR TREATED BATTING

$\text{H}_3\text{BO}_3$ %	ONE CIGARETTE		TWO CIGARETTES	
	BARE	BETWEEN 2 SHEETS	BARE	MATTRESS
	MATTRESS			
1.98	I	—	—	—
2.55	N	I	—	—
3.15	N	N	I	—
3.59	N	N	I	—
5.24	N	N	I	—
6.31	N	N	I	—
8.68	N	N	N	—

N=NO IGNITION  
 I=IGNITION

Of significance is that only a 3.15% add-on of boric acid via the vapor system permits passage of the tests requirements of the Mattress Flammability Standard FF 4-72. An add-on of 8.68% boric acid permits passage of a more severe test, the two cigarette ignition test, which is used only as a laboratory tool for evaluating different treatments.

Table II presents data demonstrating the effect of exposure time on

TABLE II  
EFFECT OF TIME ON ADD-ON AT 65°F  
MeOH-H<sub>3</sub>BO<sub>3</sub> VAPOR SYSTEM 9.4% INITIAL H<sub>2</sub>O

TIME IN MINUTES	H <sub>3</sub> BO <sub>3</sub> %	EFFICIENCY %
1	1.86	17.3
5	3.51	32.7
15	3.55	33.1
30	3.56	33.2
60	4.11	38.3
120	4.45	41.5
240	5.30	49.4
420	6.15	57.3

boric acid add-on. The initial moisture content of these samples was 9.4%. The solution temperature was maintained at 65°F. Efficiency was determined by comparing the actual boric acid add-on to that predicated by assuming all of the initial moisture present in the batting hydrolyzed available methyl borate according to the stoichiometric ratio of equation (1). It is apparent that both add-on and efficiency increase as the reaction is allowed to continue for longer exposure times.

Additional exposure time experiments were also performed with samples containing 0%, 4.9%, and 6.7% initial moisture contents. The add-on achieved and the efficiency after 5, 30, and 120 minutes are compared in Table III. It is evident that the add-on is highly dependent on the

TABLE III  
EFFECT OF INITIAL MOISTURE ON ADD-ON  
MeOH-H<sub>3</sub>BO<sub>3</sub> VAPOR SYSTEM AT 65°F

MOISTURE (INITIAL) %	H <sub>3</sub> BO <sub>3</sub> %			EFFICIENCY				
	MINUTES	5	30	120	MINUTES	5	30	120
BONE DRY	0.47	0.53	0.79	—	—	—	—	—
4.9	0.83	1.48	2.50	14.8	26.5	44.7	—	—
6.7	2.69	3.06	2.97	35.2	40.1	38.9	—	—
9.4	3.51	3.56	4.45	32.7	33.2	41.5	—	—

initial moisture content. Note that after 120 minutes of exposure the add-ons for the 4.9% and 9.4% initial moisture content are 2.50% and 4.45% respectfully, whereas their efficiencies are approximately equal. After only 5 minutes the efficiencies are considerably different. It is possible that this difference results from the immediate hydrolysis of the more accessible moisture in the high moisture samples. For the lower moisture samples, more time is needed to permit diffusion of the borates. After 120 minutes the efficiencies are comparable.

The reversible reaction forming methyl borate also yields three moles of water for each mole of borate. The addition of sulfuric acid to the solution drives the reaction to completion by scavaging the water. A series of treatments were performed where 7% by weight of sulfuric acid was added to the saturated solution. Table IV presents the data obtained.

TABLE IV  
COMPARISON OF  
MeOH-H<sub>3</sub>BO<sub>3</sub> AND MeOH-H<sub>3</sub>BO<sub>3</sub>-H<sub>2</sub>SO<sub>4</sub>  
VAPOR SYSTEMS AT 65°F

MOISTURE (INITIAL) %	H <sub>3</sub> BO <sub>3</sub> %	EFFICIENCY % (5 MINUTES)
$\text{H}_2\text{SO}_4$		
5.3	0.86	14.2
7.2	2.76	33.6
8.4	4.62	48.2
NO $\text{H}_2\text{SO}_4$		
4.9	0.83	14.8
6.7	2.69	35.2
9.4	3.51	32.7

Again the efficiency achieved increases with increased exposure time and the add-ons obtained are highly dependent upon the initial moisture content. When compared to treatments without sulfuric acid added to the treating solution there is no apparent difference through five minutes of exposure. For a fifteen minute exposure the data indicate greater efficiency with sulfuric acid in the treating solution. However, sufficient add-on to pass FF 4-72 is achieved at the shorter times and thus the addition of sulfuric acid offers no significant advantage.

Samples with an initial moisture content of 9.4% were exposed to vapors above a boiling solution of boric acid in anhydrous methanol (155 - 160°F.). Exposure times were varied from 1 to 120 minutes. Table V

TABLE V

 EFFECT OF TEMPERATURE ON ADD-ON  
 MeOH -  $H_3BO_3$  VAPOR SYSTEM 9.4% INITIAL  $H_2O$ 

TIME IN MINUTES	$H_3BO_3$		EFFICIENCY		EFFICIENCY RATIO $160^{\circ}F/65^{\circ}F$
	65°F	160°F	65°F	160°F	
1	1.86	3.51	17.3	32.6	1.9
5	3.51	5.20	32.7	48.4	1.5
15	3.55	4.98	33.1	46.4	1.4
30	3.56	4.96	33.2	46.3	1.4
60	4.11	5.21	38.3	48.5	1.3
120	4.45	5.01	41.5	46.7	1.1

compares the results to similar data obtained at 65°F. (see Table I) Note that for the same initial moisture content, a significantly greater add-on is achieved at the elevated temperature for any given exposure. The 160°F. treatment reaches maximum efficiency after only five minutes exposure. Its failure to achieve greater add-ons with time possibly results from revolatilization of the methyl borate from the treated cotton.

Sodium tetraborate decahydrate, more commonly known as borax, is not a good smolder resist compound for treating cotton batting. Application via an immersion or a dusting process results in a product which readily undergoes smoldering combustion. This results from the presence of sodium ions in the treatment which are known to catalyze combustion of carbonaceous materials. However, borax can be used effectively in the vapor phase system. Methyl borates can be generated by dissolving borax in anhydrous methanol. The addition of sulfuric acid precipitates the sodium, therefore eliminating the deleterious sodium ions. The azeotrope mixture consists of one mole of methyl borate and one mole of methanol. As seen by the reaction



the theoretical ratio of methanol to boron is 4:1, but an excess of methanol can more effectively utilize the boron in a shorter period of time.

A solution containing 0.5:16:1 ratio of borax, methanol, and sulfuric acid was prepared and allowed to equilibrate at 65°F. Two series of cotton batting samples containing 7.3 and 9.4% initial moisture content were exposed to the vapors for various times. As observed with the boric acid-methanol system the add-on and efficiency increased with exposure time and the total add-on achieved is highly dependent upon the initial moisture content. Table VI compares the add-ons and efficiencies obtained with the

TABLE VI

COMPARISON OF  
MeOH-H<sub>3</sub>BO<sub>3</sub> AND MeOH-BORAX-H<sub>2</sub>SO<sub>4</sub> AT 65°F

MOISTURE (INITIAL) %	H <sub>3</sub> BO <sub>3</sub> %			EFFICIENCY %				
	MINUTES	5	30	120	MINUTES	5	30	120
BORIC ACID								
9.4		3.51	3.56	4.45		32.7	33.2	41.5
BORAX								
9.4		3.97	6.59	6.95		36.7	60.8	64.2

methanol-borax-sulfuric and methanol-boric acid systems. The methanol-borax-sulfuric acid system is more efficient as indicated at all exposure times evaluated.

#### CONCLUSION

Treatment of cotton fiber via a deposition of boric acid from a methylborate-methanol vapor yields products that meet the Mattress Flammability Standard FF 4-72. The vapors can be generated from solution of boric acid in methanol or from solution of borax in methanol with sulfuric acid. The data indicates that the latter system is the more efficient process.

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